

THE EFFECTS OF MAJOR IMPURITIES
ON THE TRANSPORT OF HYDROGEN
THROUGH PALLADIUM

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Abstract of Dissertation Presented to the Graduate Council in
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OF HYDROGEN THROUGH PALLADIUM

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The purpose of the investigation was to study the effect of major impurities on the transport of hydrogen through solid palladium-silver electrodes.

Experimental data were to be gathered on the effect of impurities such as CO_2 , CO , N_2 and CH_4 on the transport rate with temperature, pressure and bleed rate as parameters. These impurities might be expected to be present in the effluents from ammonia or hydrocarbon reformers. The temperature range covered extended from 300°C to 460°C and pressure range from 1069 mm Hg to 2310 mm Hg.

The transport rate of pure hydrogen through 0.004 inches thick palladium-silver foil can be described by an equation of the form:

$$N_A = k_1 P^{\frac{1}{n}} \exp\left(-\frac{\Delta E}{RT}\right) = 3.8 \times 10^{-7} P^{0.60} \exp\left(-\frac{1,340}{RT}\right)$$

where N_A = transport rate in gm.moles/cm²sec.

P = pressure differential in mm Hg

R = gas constant

T = absolute temperature in $^{\circ}\text{K}$

ΔE = energy of activation

$k_1, \frac{1}{n}$ = constant

Calculation of diffusivity in the palladium-silver alloy gives an equation of the form:

$$D = 5.9 \times 10^{-3} \exp \left(- \frac{6,560}{RT} \right)$$

Comparison of this diffusivity with that for pure palladium indicates that introduction of silver lowers the diffusivity.

Introduction of impurities lowers the transport rate of hydrogen through palladium-silver foil. This can be attributed to the following effects: (1) hydrogen is diluted by the impurities; (2) impurities hinder the diffusion of hydrogen in the gas phase; (3) occupation of adsorption and dissociation sites by impurities. The overall effect of impurities is, therefore, to lower the concentration of hydrogen atoms in the upstream surface of the palladium-silver foil, and since the diffusion rate in the alloy is directly proportional to concentration, the transport rate decreases.

The transport rate of hydrogen through 0.004 inches thick 25% palladium-silver foil with impurities can be described by the following relationship at certain temperature and pressure:

$$N_A = N_{A_{\max}} \frac{B}{B - k_2} = k_1 P^{\frac{1}{n}} \exp \left(- \frac{\Delta E}{RT} \right) \frac{B}{B - k_2}$$

where $N_{A_{\max}}$ = maximum transport rate obtainable, i.e., when the bleed rate is infinite

B = bleed rate

k_1, k_2 = constant

$\frac{1}{n}$ = exponential constant

ΔE = energy of activation

Comparison of the equation for N_{Amax} with N_A for pure hydrogen shows that the value of $\frac{1}{n}$ is lower and the energy of activation ΔE is higher when impurities are present. This suggests that surface effects are present when impurities are introduced. Furthermore, the term $B/(B - k_2)$ is probably caused by effect (2). It is also expected that because of effect (1), the partial pressure of hydrogen should be used in the equation instead of total pressure.

CHAPTER I

INTRODUCTION

A. General

Since Thomas Graham (1) investigated the transport of hydrogen through palladium in 1868, numerous investigators (2,3,4) have made the same study. However, the results vary from one investigator to another, sometime as much as a thousand times. Recently, some investigators (5,6,8) have succeeded in narrowing this variability by simply using a continuous system. Previous investigators almost exclusively used static systems, which when the feed gas contains small amounts of impurities, permit the impurities to accumulate on the upstream side of the palladium membrane, thereby producing erroneous results. A continuous system bleeds part of its feed gas to the atmosphere, so that the impurities do not accumulate on the upstream side of the membrane.

The use of a continuous system does not entirely eliminate the variability of the results, for there are also other factors involved. In view of the fact that the transport of pure hydrogen through palladium is still subject to controversy, the transport of pure hydrogen has been subjected to detailed analysis. These factors which will be studied are the thermodynamics of the palladium hydrogen system, which is important for knowing the characteristics of the solubility of hydrogen in palladium; adsorption processes at the surface of the palladium, which will tell whether a certain impurity would chemisorb or physically adsorb at the surface; atomistic diffusion

mechanisms inside the solid, which deal with atomic diffusion through different crystallographic plane; and finally the effect of dislocation in the solid on the diffusion rates. Some of these discussions will be qualitative in nature, but the author trusts that they will serve as a catalyst for future research.

B. Previous Work

As mentioned previously, the transport rate of pure hydrogen in pure palladium produced numerous inconclusive data mainly because the investigators used static systems instead of continuous systems. Lombard and Eichner (8) were among the first to use a continuous system for obtaining data; however, their transport rates were very or relatively low owing to contamination of the membrane by brazing with silver solder. Darling (7) using commercial hydrogen showed that, for a static system, the transport rate decreased rapidly with time; he attributed these results to the fact that impurities blocked the entrance of hydrogen at the surface. When a bleed was imposed, the transport rate did not vary with time, thus lending evidence to his thesis.

Hurlbert and Konecny (5), using a continuous system, observed that surface reaction is not the rate-limiting process for membranes thicker than 20 microns. DeRosset (6) used pure palladium to study the transport rate of impure feed gas with an upstream pressure of 1-700 psig and a downstream pressure of 0-300 psig.

Commercially, Engelhard Industries (9) and Milton Roy both use palladium-silver alloy as the separation barrier for their small scale hydrogen purifier. Union Carbide (10) has constructed a large

scale hydrogen purifier using palladium as membrane, but few operating data are given. A mixed feedstock of gases can be used in all of these commercial hydrogen purifiers.

Pure palladium membranes have the disadvantage of cracking and distorting when used for a long time, especially when the membrane is cycled through heating and cooling in an atmosphere of hydrogen. However, Union Carbide uses its palladium membrane continuously without shutting down, and the life of the palladium is, therefore, prolonged. Pure palladium usually results in a higher transport rate at high pressures and medium temperature than palladium-silver alloy, because the maximum solubility of hydrogen in pure palladium is greater than palladium-silver alloy. Engelhard Industries and Milton Roy utilize a palladium-silver alloy in their diffuser. Since these units are usually small and are often shut off and turn on, the palladium alloy has an edge over pure palladium.

The bulk of the measurements of hydrogen transport through palladium are for pure palladium membranes and for a downstream pressure of greater than an atmosphere. When divergent results were obtained by the investigator for the transport of hydrogen through palladium usually qualitative explanations were given.

McBride and McKinley (10) found that when carbon monoxide, methane, or hydrogen sulfides were present in the feedstock, they reacted with palladium at a temperature slightly above 400°C to form palladium carbides and at a lower temperature to form palladium sulfides. Hurlbert and Konecny (5) observed sulfide formation at around 350°C . Several investigators (5,11) noticed that air will

reactivate a poisoned palladium membrane when heated at high temperature; this the author believed to be a removal of poison by oxidation. The palladium oxide formed in this case can be easily removed when the membrane is exposed to an atmosphere of hydrogen, and this process will be examined thermodynamically in a later section. There also exists a possibility that carbon is deposited as a result of a dehydrogenation process, in which the surface carbon may also diffuse inside the metal, thus further poisoning the membrane.

C. Statement of the Problem

The primary object of this investigation was to study the effect of major impurities on the transport of hydrogen through solid palladium-silver electrodes. Hydrogen-oxygen fuel cells generally use porous material as electrodes and pure hydrogen as fuel. The use of solid electrodes has the advantage of preventing the penetration of the electrolyte into the electrode. The use of impure hydrogen as fuel would reduce the operating cost considerably.

Experimental data were to be gathered on the effect of impurities such as CO_2 , CO , N_2 , and CH_4 on the transport rate with temperature, pressure and bleed rate as parameters. These impurities might be expected to be present in substantial quantities in the effluents from ammonia or hydrocarbon reformers. The temperature range covered extended from 300°C to 460°C and pressure range from 1069 mm Hg to 2310 mm Hg.

CHAPTER II

THEORY

A. Thermodynamics of the Pd-H and Pd-Ag-H Systems

The rate of diffusion of hydrogen through palladium is directly proportional to the solubility of hydrogen in palladium. Since the equilibrium isotherms give information on solubility as well as on phase transitions, it is therefore important to know the characteristics of these equilibrium isotherms. Information on phase transitions is valuable since the diffusion coefficient changes when a phase change occurs.

Sieverts and co-workers (12,13,14) found that hydrogen adsorbed in palladium according to $P^{1/2}$ law at high temperature and low pressure. This suggested that hydrogen molecules dissociate into atoms before entering the crystal lattice, indicating that hydrogen possibly exists in palladium as atoms. However, Norberg (15) and Isenberg (16) proved experimentally and theoretically that hydrogen exists in the palladium lattice as quasi-free protons. The electrons are attached more closely to palladium atoms than to the proton.

Paramagnetic susceptibility studies (17) show that susceptibility decreases with the amount of hydrogen absorbed and drops to zero when there are about 0.55 hydrogen atom per palladium atom. This is attributed to the hydrogen electron going into the d shell of the palladium atom, decreasing the number of positive holes and hence the paramagnetism.

Gillespie and Galstaun (18) obtained the equilibrium

isotherms for the Pd-H system shown in Figure 1. It may be observed that at a constant temperature and at low pressure, the solubility of hydrogen increases as pressure increases, Section A to B in Figure 1. At point B the curve becomes horizontal, indicating that the solubility increases even though the pressure remains constant. This increase in solubility at constant pressure continues until a point is reached when an increase in pressure is again necessary to increase the solubility, as shown in Section CD in Figure 1. The first portion of the isotherm AB represents an α -phase, the horizontal portion BC indicates an α - β phase transition, while the last portion of the curve, CD, represents the β -phase.

The length of the α - β phase transition decreases as the temperature increases and finally disappears altogether. The temperature and pressure where it just disappears is called the critical point, and for the palladium-hydrogen system it is around 20 atmospheres and 295°C.

Nace and Aston (19,20) studied the heat capacity of Pd_2H at low temperatures ranging from 16 to 340°K and found that tetrahedral PdH_4 is formed at a temperature of less than 50°K. The PdH_4 structure is located at the corner of the palladium lattice. At temperatures higher than 50°K the PdH_4 structure dissociates into simpler hydride, and at room temperature this model will be indistinguishable from the quasi-free proton model. It can be concluded, therefore, that above room temperature, the protons are distributed randomly at the interstitial sites.

The lattice parameter of the α -phase is 3.983Å; this expands to

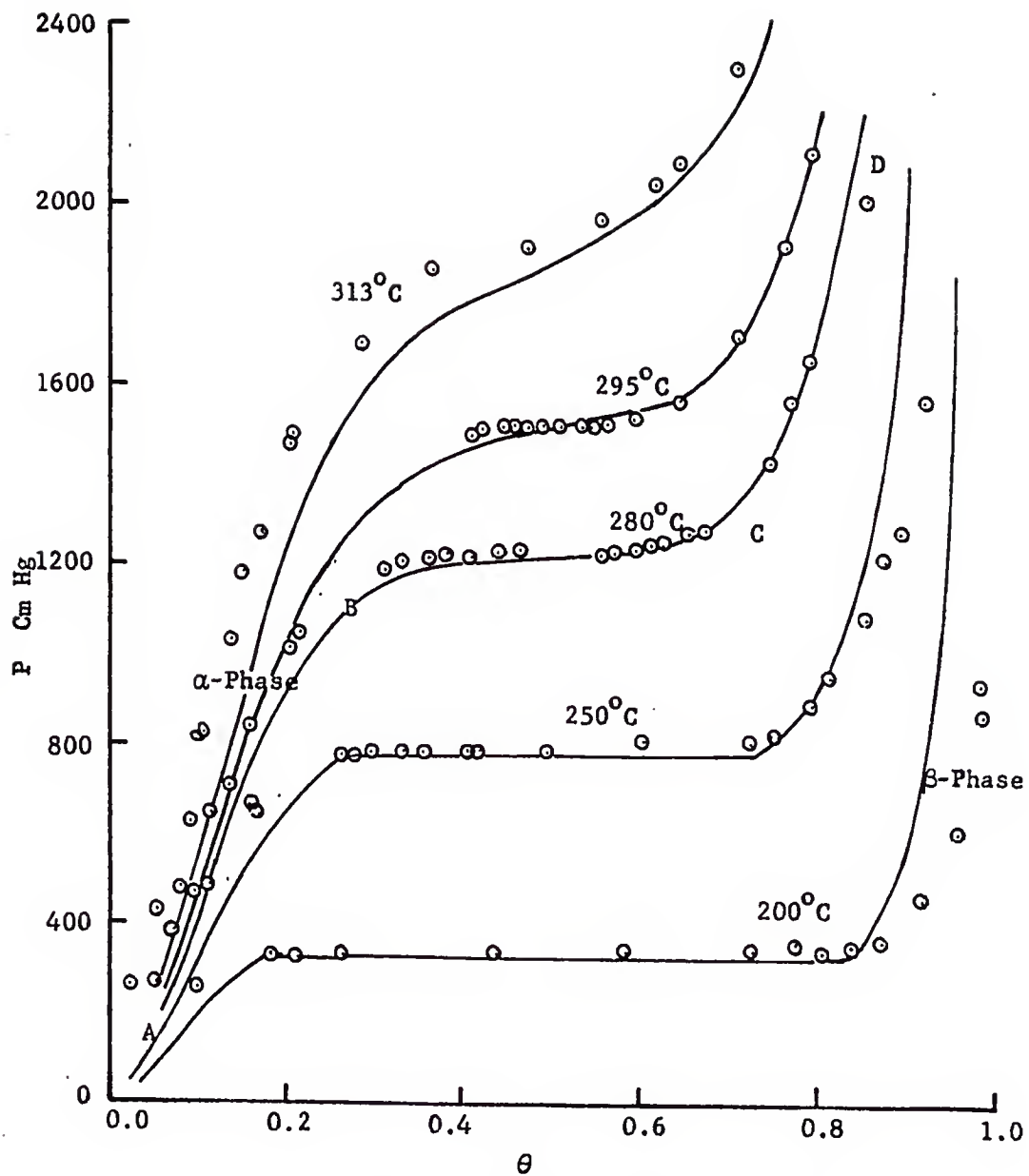


Figure 1. Equilibrium Isotherm
for the Pd-H Systems

4.025 $\text{\AA}$ ⁰ for the β -phase.

To improve the mechanical properties of the palladium membrane in an atmosphere of hydrogen, palladium is alloyed with silver. Introduction of silver into the palladium lattice changes the equilibrium isotherm. Although the equilibrium isotherm for the Pd-Ag-H systems is similar in shape to the Pd-H system, the critical point is lower and the maximum solubility is less than for pure palladium. It was mentioned earlier that the electron of the hydrogen atom goes into the d-band of the palladium atom. Since the added silver atoms fill some of the d-band vacancies in the palladium atoms with their own electron, it will decrease the maximum solubility of hydrogen in the alloy. However, in the α -phase region at low temperature, hydrogen is more soluble in the alloy than in pure palladium. Figure 2 (39) shows this characteristic for a 25 $^{\circ}\text{C}$ isotherm. It may be noted that for this particular isotherm, the equilibrium pressure of hydrogen for the α - β phase transition diminishes with increase in silver content up to 30 per cent. Very few data are available for the Pd-Ag-H system, especially at high temperature.

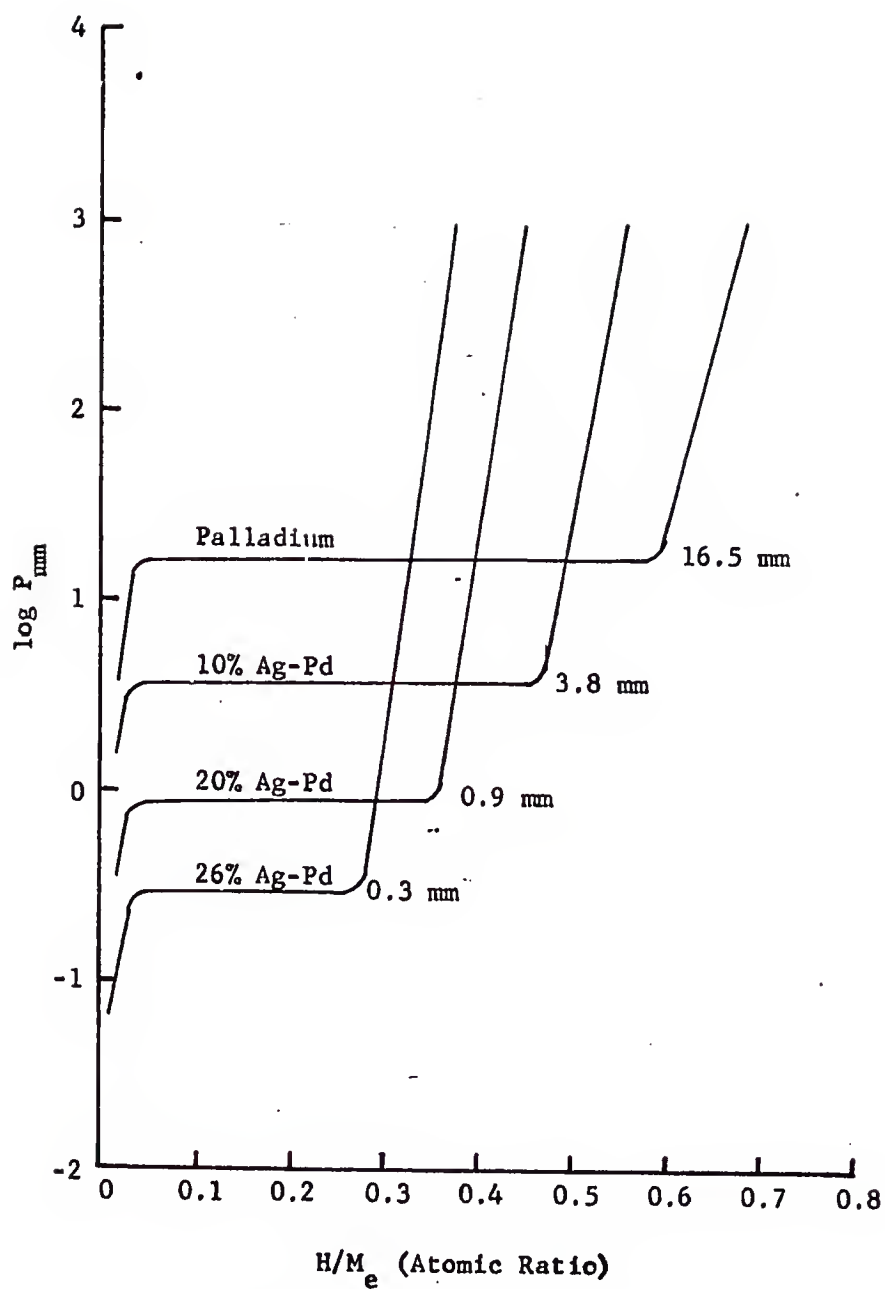


Figure 2. Equilibrium Isotherms
for Ag-Pd-H System at 25°C

B. Statistical Thermodynamics and Equilibrium Isotherms

Lacher (21) obtained a theoretical equation for the equilibrium isotherms by statistical thermodynamics based on an interstitial hydrogen model. Libowitz (22) arrived at a similar equation using a vacancy model. However, the Lacher model is a better model since it is based on a realistic quasi-free proton model which has been confirmed by several investigators.

Here an equation will be derived which is a combination of the models used by Lacher and Fowler (21,37). The assumptions made in the derivation are:

(1) There is a fixed number of interstitial sites, N_g , where the hydrogen atom can be absorbed.

(2) The energy of interaction between a pair of nearest neighbors of hydrogen is equal for all pairs.

Let the number of pairs of neighboring hydrogen atoms in a particular configuration be N_{HH} , and let $\frac{2N_{HH}\epsilon_{HH}}{z}$ be its interaction energy. Then from statistical thermodynamics (37), the expression for the partition function for this system will be:

$$Q = \sum_{N_{HH}} g(N_H, N_{HH}) \exp^{-N_{HH} \frac{2\epsilon_{HH}}{zkT}} \left[a_H(T) \right]^{N_H} \quad (1)$$

where Q = partition function

$g(N_H, N_{HH})$ = total number of distinguishable configurations of N_H atoms

z = number of nearest neighbors

N_H = number of hydrogen atoms in the lattice.

ϵ_{HH} = total interaction energy at saturation per atom

k = Boltzmann Constant

T = temperature

$a_H(T)$ = the partition function for the internal degree of freedom of an absorbed hydrogen atom referred to the ground state at infinite separation

Defining $\bar{N}_{HH}$ by Equation (2)

$$\begin{aligned} \exp^{-\bar{N}_{HH} 2\epsilon_{HH}/zkT} \sum_{N_{HH}} g(N_H, N_{HH}) \\ = \sum_{N_{HH}} g(N_H, N_{HH}) \exp^{-N_{HH} 2\epsilon_{HH}/zkT} \end{aligned} \quad (2)$$

Substituting Equation (2) into (1) the partition function will be in the form

$$Q = \left[a_H(T) \right]^{N_A} \exp^{-\bar{N}_{HH} 2\epsilon_{HH}/zkT} \sum_{N_{HH}} g(N_H, N_{HH}) \quad (3)$$

but

$$\sum_{N_{HH}} g(N_H, N_{HH}) = \frac{N_s!}{N_H! (N_s - N_H)!} \quad (4)$$

therefore, Equation (3) becomes

$$Q = \left[a_H(T) \right]^{N_H} \exp^{-\bar{N}_{HH} 2\epsilon_{HH}/zkT} \frac{N_s!}{N_H! (N_s - N_H)!} \quad (5)$$

From statistical thermodynamics the Helmholtz free energy, F , can be written as:

$$F = - kT \ln Q \quad (6)$$

Substituting the value of Q from Equation (5) to equation

(6) and using Sterling's approximation

$$\begin{aligned} F/kT = & -N_s \ln N_s + N_H \ln N_H + (N_s - N_H) \ln(N_s - N_H) - N_H \ln a_H(T) \\ & + \bar{N}_{HH} 2\epsilon_{HH}/zkT \end{aligned} \quad (7)$$

The equilibrium or average value of N_{HH} can be expressed from statistical thermodynamics as:

$$\bar{N}_{HH} = \frac{\sum_{N_{HH}} N_{HH} g(N_H, N_{HH}) \exp^{-N_{HH} 2\epsilon_{HH}/zkT}}{\sum_{N_{HH}} g(N_H, N_{HH}) \exp^{-N_{HH} 2\epsilon_{HH}/zkT}} \quad (8)$$

Each occupied site has z neighbors, and with perfectly random arrangements each site has a probability $\frac{N_H}{N_s}$ of being occupied. Therefore the average number of neighbors of any given N_H is $z \frac{N_H}{N_s}$. The total equilibrium number of pairs of neighbors will be:

$$\bar{N}_{HH} = \left(\frac{1}{2} N_H \right) \left(z \frac{N_H}{N_s} \right) = \frac{1}{2} z \frac{N_H^2}{N_s} \quad (9)$$

But $\bar{N}_{HH} = \bar{\bar{N}}_{HH}$ for random distributions (38); therefore Equation (9) becomes

$$\begin{aligned} \frac{F}{kT} = & -N_s \ln N_s + N_H \ln N_H + (N_s - N_H) \ln(N_s - N_H) - N_H \ln a_H(T) \\ & + \frac{N_H^2 \epsilon_{HH}}{N_s kT} \end{aligned} \quad (10)$$

The chemical potential can be written as:

$$\mu = \left(\frac{\partial F}{\partial N_H} \right)_{T, N_s} = kT \left[\ln \frac{N_H}{N_s - N_H} - \ln a_H(T) + \frac{N_H}{N_s} \frac{2\epsilon_{HH}}{k} \right]$$

$$= kT \left[\ln \frac{\theta}{1 - \theta} - \ln a_H(T) + \frac{2\theta\epsilon_{HH}}{kT} \right] \quad (11)$$

where $\theta = \frac{N_H}{N_s}$ the fraction of sites occupied but

$$a_H(T) = \exp^{-\epsilon_H/kT} q_H(T)\rho \quad (12)$$

where

$(-\epsilon_H)$ is the energy required to remove an absorbed H atom, far removed from any other absorbed H-atoms, from its lowest state in the metal to rest at infinite dispersion.

$q_H(T)$ is the partition function for vibration of absorbed H atom relative to the lattice.

ρ is the spin weight of the proton.

Defining λ_H as the absolute activity and using Equation (12)

$$\lambda_H(S) = \exp^{\mu/kT} = \frac{\theta}{1 - \theta} \frac{\exp^{\frac{\epsilon_H + 2\theta\epsilon_{HH}}{kT}}}{q_H(T)\rho} \quad (13)$$

The absolute activity in the gas phase consisting entirely of diatomic molecules of hydrogen at a pressure p is:

$$\lambda_H(G) = \left(\frac{p}{kT} \right)^{1/2} \exp^{-1/2 \epsilon_D/kT} \times \left\{ \frac{(2\pi 2M_H kT)^{3/2}}{h^3} \times \frac{8\pi^2 M_I kT \rho^2}{2h^2} \right\}^{-1/2} \quad (14)$$

where ϵ_D = energy required to dissociate a hydrogen molecule from its lowest state into two free H-atoms each in its lowest state.

M_H = atomic mass of hydrogen

h = Planck Constant

M_I = moment of inertia of the hydrogen molecule.

Equating Equations (13) and (14)

$$P = \left(\frac{\theta}{1 - \theta} \right)^2 kT \exp^{2(\epsilon_H + 2\epsilon_{HH} + \frac{1}{2}\epsilon_D)k/T} \times \frac{(2\pi 2M_H kT)^{3/2}}{h^3} \times \frac{8\pi^2 M_I kT}{2h^2 \{q_H(T)\}^2} \quad (15)$$

Let $P\left(\frac{1}{2}\right)$ be defined by Equation (16)

$$P\left(\frac{1}{2}\right) = \frac{kT}{\{q_H(T)\}^2} \frac{(2\pi 2M_H kT)^{3/2}}{h^3} \frac{8\pi^2 M_I kT}{2h^2} \exp^{\frac{2(\epsilon_H + \epsilon_{HH} + \frac{1}{2}\epsilon_D)}{kT}} \\ = K(T) \exp^{2(\epsilon_H + \epsilon_{HH} + \frac{1}{2}\epsilon_D)/kT} \quad (16)$$

where

$$K(T) = \frac{kT}{\{q_H(T)\}^2} \frac{(2\pi 2M_H kT)^{3/2}}{h^3} \frac{8\pi^2 M_I kT}{2h^2} \quad (17)$$

Therefore Equation (15) will be simplified to:

$$P = P\left(\frac{1}{2}\right) \left(\frac{\theta}{1 - \theta} \right)^2 \exp^{(2\theta - 1)2\epsilon_{HH}/kT} \quad (18)$$

If $\epsilon_{HH} < 0$, there will be a critical temperature given by:

$$-\epsilon_{HH}/kT_c = 2 \quad (19)$$

T_c = critical temperature

It is not possible to determine theoretically all of the parameters in Equation (15), therefore experimental data must be obtained to evaluate these constants. To do this it is convenient to convert Equations (16), (18) and (19) to a molal basis.

$$P\left(\frac{1}{2}\right) = K'(T) \exp^{2(E_H + E_{HH} + \frac{1}{2} E_D)/RT} \quad (20)$$

$$P = P\left(\frac{1}{2}\right) \left(\frac{\theta}{1-\theta}\right)^2 \exp^{(2\theta-1)2E_{HH}/RT} \quad (21)$$

$$-E_{HH}/RT_c = 2 \quad (22)$$

The constants $K'(T)$ and $E_H + E_{HH} + \frac{1}{2} E_D$ are obtained from the plot of $\ln P\left(\frac{1}{2}\right)$ versus $\frac{1}{T}$. While E_{HH} is obtained from the critical temperature by using Equation (22).

Lacher (21) obtained the following equation similar to equation (20)

$$\log P_{\text{mm}}\left(\frac{1}{2}\right) = 7.4826 - \frac{1877.82}{T} \quad (23)$$

He also found that $T_c = 568^\circ\text{K}$, so that $E_{HH} = -2(R)(568)$. Taking the log of Equation (21) and substituting the corresponding value of E_{HH} one obtains

$$\log P_{\text{mm}} = \log P_{\text{mm}}\left(\frac{1}{2}\right) + 2\log \frac{\theta}{1-\theta} - \frac{986.7(2\theta-1)}{T} \quad (24)$$

On inserting Lacher's value for $\log P\left(\frac{1}{2}\right)$ Equation (24) becomes

$$\begin{aligned} \log P_{\text{mm}} &= 7.4826 - \frac{1877.82}{T} + 2\log \frac{\theta}{1-\theta} - \frac{986.7(2\theta-1)}{T} \\ &= 7.4826 + 2\log \frac{\theta}{1-\theta} - \frac{891.2 + 1973.4\theta}{T} \end{aligned} \quad (25)$$

Equation (25) is plotted in Figure 1 along with typical experimental data. It can be seen that Equation (25) correlates very well with the data.

Equation (25) is obtained by using pure palladium data,

therefore it cannot be used for the palladium-silver alloy. However, the few experimental data available for the palladium-silver alloy suggest a similar pattern. Since there is a lack of data for the whole range of the equilibrium isotherms for the palladium-silver-hydrogen system, an extrapolation method will be used to predict these equilibrium isotherms.

The equilibrium isotherms for the Pd-Ag-H system at 25°C for several silver contents were shown in Figure 2. It can be seen that the equilibrium pressure for the α - β phase transition decreases in proportion to the silver content. This phenomenon can be used to predict some of the constants in Equation (21) for the Pd-Ag-H system.

In Figure 3 a plot of $\log P_{\text{mm}} \left(\frac{1}{2} \right)$ versus the silver content of the alloy obtained from Figure 2 at 25°C yields the following relationship

$$\log P_{\text{mm}} = 1.2165 - 6.52X_{\text{Ag}} \quad (26)$$

where X_{Ag} is weight fraction of silver.

Assuming that this relation applies also to other temperatures, so that

$$\frac{a}{T} \approx 6.52 \quad \text{when } T = 298^\circ\text{C} \quad (27)$$

$$a = 1942$$

and

$$\begin{aligned} \log \bar{P}_{\text{mm}} \left(\frac{1}{2} \right) &= 1.2165 - \frac{1942}{T} X_{\text{Ag}} \\ &= \log P_{\text{mm}} \left(\frac{1}{2} \right) - \frac{1942}{T} X_{\text{Ag}} \end{aligned} \quad (28)$$

Inserting this value for $\log \bar{P}_{\text{mm}} \left(\frac{1}{2} \right)$ in Equation (23) we obtain

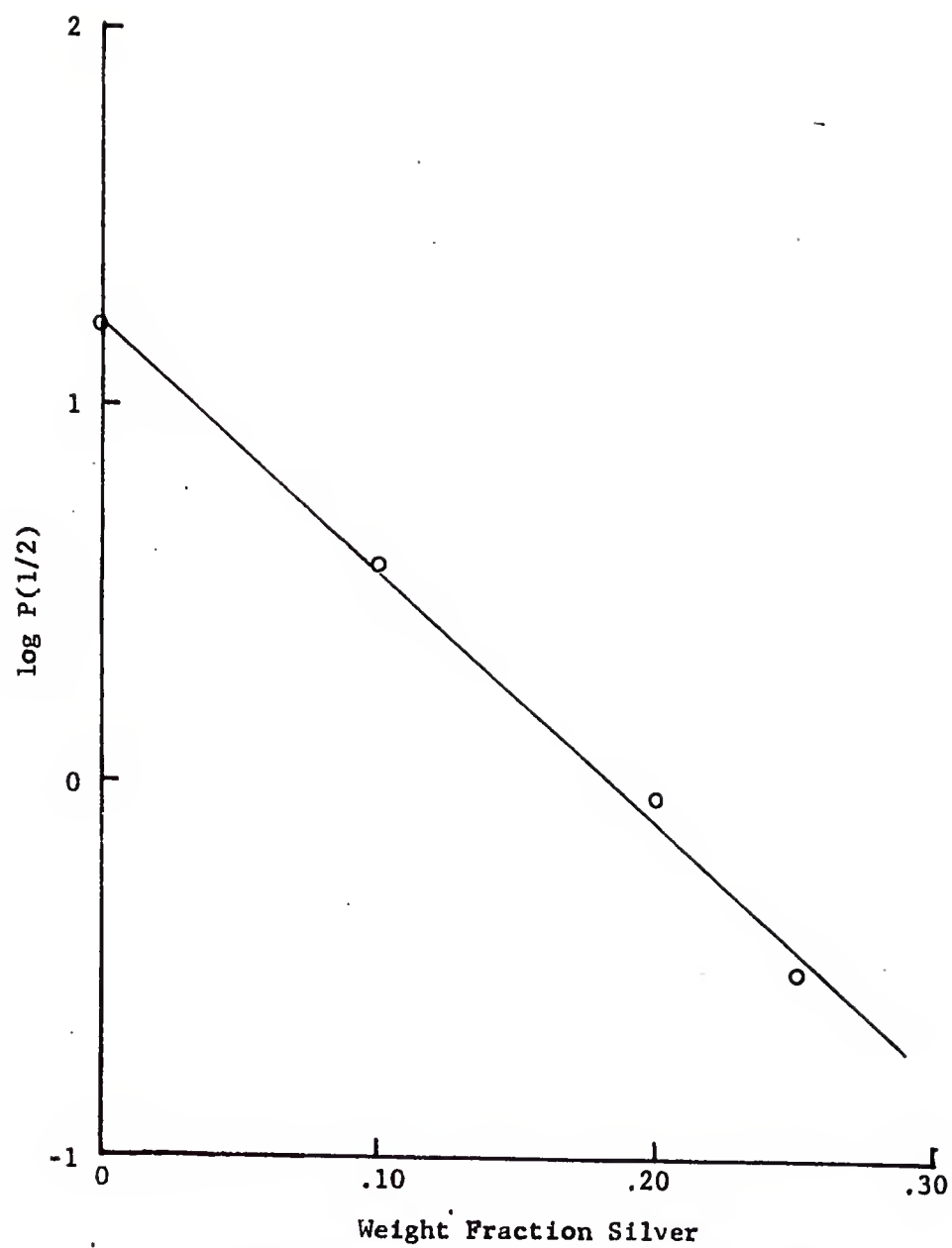


Figure 3. Logarithm of the Equilibrium Pressure Versus Silver Content

$$\begin{aligned} \log \bar{P}_{\text{mm}} \left(\frac{1}{2} \right) &= 7.4826 - \frac{1877.82}{T} - \frac{1942}{T} X_{\text{Ag}} \\ &\approx 7.4826 - \frac{1877.82(1 + X_{\text{Ag}})}{T} \end{aligned} \quad (29)$$

For the prediction of $\bar{E}_{\text{HH}}$ for the Pd-Ag-H system, a plot of T_c versus X_{Ag} is made. Only two points are known for this plot; one of the points is obtained from the data on the 30% Ag of Makrides (23), and the other is for pure palladium. Assuming a straight line relationship Figure 4 was constructed.

One conclusion which can be shown from Figure 4 is that $\bar{E}_{\text{HH}}$ decreases as the amount of silver increases. This can be explained by the fact that the total interaction energy at saturation per mole will decrease because the solubility of hydrogen is decreased by the addition of silver. Makrides (23) used the ratio of maximum solubility of hydrogen in alloy to that in palladium to correct the value of $\bar{E}_{\text{HH}}$ in the alloy.

The value of T_c for the 25% silver alloy is about 350°K; therefore the equilibrium isotherm expression for the 25% silver alloy will be:

$$\log \bar{P}_{\text{mm}} = 7.4826 + 2 \log \frac{\theta}{1 - \theta} - \frac{1635.52 + 1218\theta}{T} \quad (30)$$

C. Transport of Hydrogen Through Palladium

The transport of hydrogen through palladium can be attributed to the following series of processes:

- (1) The hydrogen gas molecule is adsorbed and dissociates into hydrogen atoms at the upstream surface.

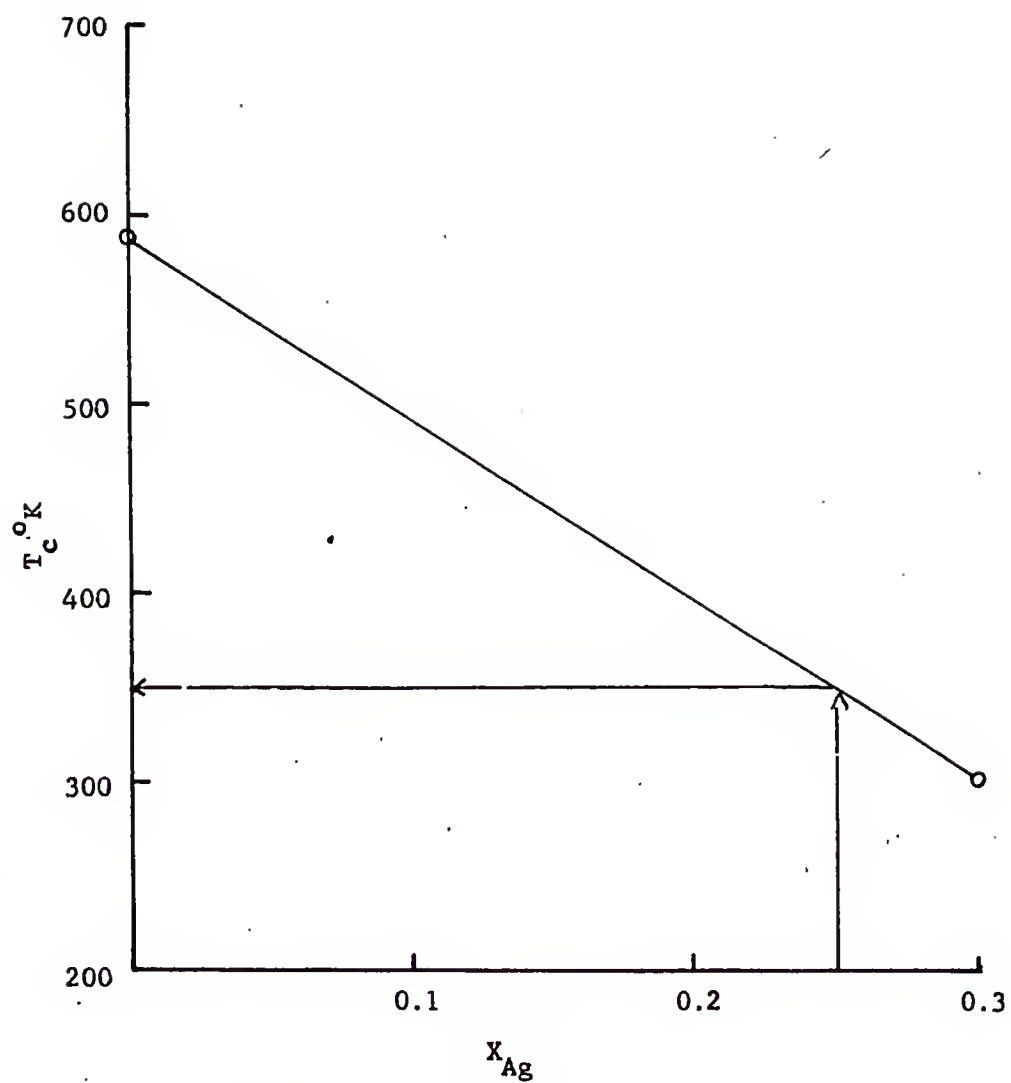


Figure 4. A Plot of Critical Temperature Versus Silver Content

(2) The adsorbed hydrogen atom enters into the crystal lattice and becomes a proton and a quasi-free electron.

(3) The proton diffuses through the palladium lattice.

(4) At the downstream surface the proton recombines with an electron to form a hydrogen atom.

(5) Two hydrogen atoms combine to form a hydrogen molecule.

(6) Hydrogen molecules desorb from the downstream surface.

Each of the steps above may be the rate-controlling one; it is therefore important to discuss them separately.

1. The Adsorption and Dissociation of Hydrogen in the Palladium Surface

The hydrogen molecule before diffusing through the metal must first adsorb in the metal surface and subsequently dissociate into two hydrogen atoms. Adsorption processes can be broadly divided into two types depending on the amount of heat evolved during adsorption; these are (1) physical adsorption, (2) chemisorption.

The heat of chemisorption is generally higher than the heat of physical adsorption, since in chemisorption chemical bonds appear to be formed between the gas and metal atom. In physical adsorption van de Waals forces are the forces acting between molecules, and these are generally small; thus the heat evolved is generally small. Electrochemical determination of the heat of adsorption of hydrogen on finely divided palladium shows a heat of adsorption of 27.5 kcal/mole (24), which is in the range of chemisorption.

Chemisorption is usually the first step toward the dissociation of the hydrogen molecule on metal surfaces; it is found to be

true especially in heterogeneous catalytic chemical reactions.

The conditions in which surface effects determine the rate of diffusion are the following:

- (1) low pressure and low temperature,
- (2) very thin membrane,
- (3) blocking and poisoning of the surface by impurities,
- (4) physical condition of the surface.

Hydrogen molecules are adsorbed and dissociated on certain active sites in the metal surface, the number of molecules adsorbed and dissociated being proportional to the product of the number of molecules striking the surface and the probability of adsorption and dissociation. This condition therefore requires relatively high pressure and temperature. At low pressure the number of molecules striking is greatly reduced, resulting in a reduction of the transport rate. The rate of dissociation increases exponentially with temperature, and proportionally with square root of pressure. This means that temperature should produce more profound effect than pressure.

The surface effect will also be the rate-controlling factor if the thickness of the metal membrane is greatly reduced so that the resistance to flow offered by the metal membrane is negligible compared to that of the surface. This means that the metal membrane will diffuse all the gases that the surface has dissociated. Hurlbert and Konecny (5) found that at upstream pressures of 1 to 7 atmospheres and temperature around 350°C, surface effects are rate-limiting for membranes thinner than 20 micron. This limiting thickness, of course,

will vary for different temperatures and pressures.

The blocking and poisoning of the surface by impurities is caused by occupation of the active sites by foreign atoms (25,26).

The following kinds of substances can cause poisoning:

- (1) impurities in the feed gas,
- (2) vaporized metal,
- (3) impurities in the metal,
- (4) metal oxide formation.

Impurities in the feed gas, such as hydrocarbon vapor and hydrogen sulfide, decrease the transport rate greatly at temperatures in the range 400°C to 600°C (25). This was explained by McBride (10) as caused by the chemical reaction of these two gases with palladium forming palladium sulfide or carbide. The formation of palladium sulfide is instantaneous and irreversible. The formation of palladium carbide may involve a more complicated reaction, and may be a very slow process; furthermore the carbon atoms at the surface may diffuse into the palladium lattice, thereby further decreasing the transport rate.

Oxygen and water react with palladium to form palladium oxide. If an atmosphere of hydrogen gas is introduced, the following reaction will occur



From thermodynamics

$$\log K = -\Delta F^{\text{of}}/2.3RT \quad (32)$$

where K = the equilibrium constant for a reaction.

ΔF^{of} = the free energy of formation at 298°K in cal/mole.

For the reaction above

$$\begin{aligned}\Delta F^{\text{of}} &= \Delta F^{\text{f}}(\text{product}) - \Delta F^{\text{f}}(\text{reactant}) \\ &= -54.64 - (-13.45) = -41.19 \text{ kcal.}\end{aligned}$$

Substituting the value of ΔF^{f} and a temperature of 623°K to equation (32)

$$\log K = 14.5$$

$$K = 3.2 \times 10^{14}$$

$$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = 3.2 \times 10^{14} \quad (33)$$

Therefore

$$P_{\text{H}_2} = 5 \times 10^{-5} P_{\text{H}_2\text{O}}$$

Therefore if the vapor pressure of water is around 23 mm Hg, the corresponding equilibrium pressure for hydrogen will be 1.2×10^{-13} mm Hg; since the pressure of hydrogen is usually above 760 mm Hg, it can be concluded that all of the PdO will be converted to palladium.

Similarly for the silver, the reaction will be



$$P_{\text{H}_2} = 1.2 \times 10^{-12} P_{\text{H}_2\text{O}}$$

From this it can be concluded that no Ag_2O will exist when a hydrogen pressure of more than 760 mm is present.

Many investigators have found that an inactive palladium membrane can be reactivated by heating in an atmosphere of air;

however, this method does not produce a lasting effect. Recently, the use of low energy electron diffraction (27) has led to some understanding of the situation when certain gases are adsorbed on the metal surface. It was found that the surface atoms rearrange when a gas is adsorbed. The adsorption of oxygen on nickel, for example, causes rearrangement of all three crystallographic planes of nickel (100, 110, 111 surfaces). Since palladium is similar to nickel in crystalline structure, i.e., both are face centered cubic and both are transition metals, it seems reasonable to assume that adsorption of oxygen causes surface rearrangement. In these circumstances the transport rate will be relatively high at the start; then when the surface rearranges to the equilibrium configuration, the transport rate will decrease. This was observed by Makrides (23), but he offered a different explanation, namely that the decrease in transport rate was caused by impurities.

When the diffusion cell is operated at high temperatures some of the metal may be vaporized and is deposited on the surface of the membrane. This would be expected to decrease the transport rate. Such metals as lead and iron in the form of FeCl_3 can poison the palladium membrane. Surface diffusion of foreign atoms from the vicinity of the palladium membrane, such as copper gasket, also slows down the transport rate.

Assuming that there is no effect exerted by neighboring molecules, the time in which a molecule stays at the surface can be predicted from the heats of adsorption and the physical properties of the metal. This residence time of the molecule at the surface can

be used as a measure of the poisoning effect of certain molecules.

According to De Boer (28) the adsorption time of a molecule in the surface is given by:

$$\tau = \tau_0 \exp \frac{\Delta H}{RT} \quad (35)$$

$$\text{where } \tau_0 = 4.75 \times 10^{-13} \frac{MV^{2/3}}{T_s} \quad (36)$$

τ = time of adsorption

M = mean molecular weight per constituent atom

V = molar volume in cm^3

T_s = melting temperature $^{\circ}\text{K}$

T = temperature $^{\circ}\text{K}$

R = gas constant, $\text{cal/mole}^{\circ}\text{K}$

ΔH = heats of adsorption, cal

The residence time for hydrogen on palladium at room temperature is about 10^{-2} secs. If a gas has a much larger adsorption time than hydrogen, then the gas can be said to be a poison.

Trapnell (29) indicated that unsaturated hydrocarbons, such as ethylene, chemisorbed on the transition metals according to the equation:



The heat of adsorption in this case can be estimated by using Pauling's (30) equation for single bond energies.

$$E(X - Y) = \frac{1}{2} E(X - X) + E(Y - Y) + 2.306(\mu_X - \mu_Y)^2 \quad (38)$$

where $E(X - Y)$ is the bond energy between X and Y

μ_X is the electronegativity.

The initial heat of chemisorption q_0 can now be written as:

$$q_0 = 2E(\text{Pd-Pd}) + E(\text{H-H}) + E(\text{C-C}) - 2E(\text{C-H}) \\ + 46.12(\mu_{\text{Pd-C}}^2 + \mu_{\text{Pd-H}}^2) \quad (39)$$

Substituting the values

$$E(\text{Pd-Pd}) = 15.5$$

$$E(\text{H-H}) = 104.2$$

$$E(\text{C-C}) = 83.1$$

$$E(\text{C-H}) = 98.8$$

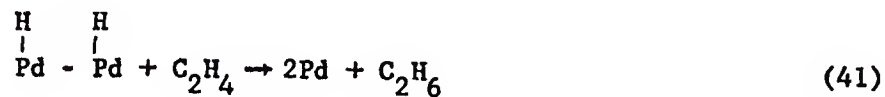
$$\mu_{\text{Pd-C}}^2 = 0.09$$

$$\mu_{\text{Pd-H}}^2 = 0.01$$

one obtains a value q_0 of 22.5 kcal and an adsorption time of 4×10^3 secs. Similarly, this approach yields an adsorption time for hydrogen of 4×10^{-2} secs. Therefore it can be concluded that for an equal mole fraction of hydrogen and ethylene at room temperature, the ethylene will be adsorbed more than hydrogen. However, the acetylinic complex formed in Equation (37) is slowly removed by gaseous hydrogen, presumably as ethylene:



or



2. The Diffusion of Hydrogen in the Palladium Lattice

There are several theories which attempt to explain the absorption of hydrogen in palladium and the mechanism of its diffusion through the palladium lattice. Some of these theories are:

- (1) A chemical compound is formed when hydrogen is absorbed in the palladium lattice.
- (2) Hydrogen is rift occluded in the palladium lattice.
- (3) Hydrogen forms an interstitial solution either as atoms or protons in the palladium lattice.

Simons and Ham (31) considered the diffusion of gases through metal as pure chemical phenomenon, i.e., a chemical compound is formed between the gas and the metal. This theory would suggest that diffusion of hydrogen is accomplished by the kinetic dissociation of the compound, and, since a concentration gradient exists in the metal membrane, the movement of hydrogen will be toward the low pressure side. This theory may be valid if the bond between the metal and gas is sufficiently strong to consider it a compound. However, since hydrogen diffuses through palladium quite rapidly at elevated temperatures, it appears that this mechanism is of minor importance. Nace (19,20) has suggested that chemical bonds are formed between the hydrogen and palladium. The hydrogen diffuses through palladium in this case is assumed to occur as the movement of hydrogen atoms by the following mechanism: (1) rotation about a parent palladium atom; (2) bonding to, and subsequent rotation about a neighboring atom. When the temperature is raised to room temperature, the bonds are broken, and the hydrogen atoms are randomly distributed so that an interstitial solution is formed.

Smith (32) believes that hydrogen diffuses through palladium via rifts, a rift being a deformed or dislocated portion of the metal crystal possessing a great ionization power because of imbalanced forces in the stressed metal. This theory was concluded to explain the greater solubilities and diffusion rates observed when the metal is deformed by cold working. It is believed that the formation of rifts, as shown by line-broadening in the X-ray diffraction spectra, causes hydrogen to be occluded in the metal. Kydonius (33) found that sonic vibration increased the rate of mass transfer through palladium by producing dislocations. It would be hazardous to assume that the mechanism of diffusion is mainly through rifts in dislocation. Because if this is true, other metals such as nickel and copper can be made to have the same transport rate as that of palladium; this has never been accomplished experimentally. The probable reason for the increase in the absorption or diffusion rate in stressed metal is that in stressed metal the dislocations serve as a reservoir for the hydrogen and at the surface dislocation increases the surface activity. However, the majority of hydrogen appears to diffuse interstitially.

The diffusion of hydrogen in the palladium lattice can be described from an atomistic point of view. It was shown earlier that the proton occupies certain interstitial sites in the palladium lattice, the most probable sites being those shown in Figure 5. These sites are located at the edges and at the center of the face-centered cubic lattice.

Diffusion appears to involve hydrogen jumping from one interstitial site to another. From these considerations an equation can be

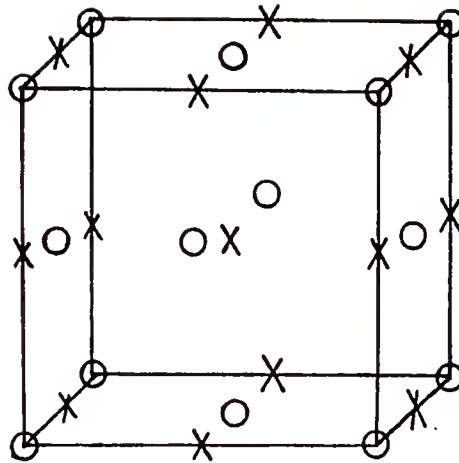


Figure 5. Interstitial Sites for a Face Center Cubic Lattice.
O Indicates Metal Atom, X Indicates the Interstitial Position

derived to describe these processes (40,41): Consider the interstitial position of a face-centered cubic lattice as shown in Figure 6. Three atomic planes are drawn in this figure separated by a distance of λ . Assume that there exists a concentration gradient of hydrogen along the x axis which is perpendicular to the (001) atomic plane. A hydrogen in an interstitial position may jump in forward, backward, or in a direction perpendicular to the x -axis. Let P_r be the probability for a given interstitial hydrogen to make a jump per second and $f_r P_r$ be the probability for a jump per second in the forward direction. Also assume the probability for a forward and backward jump to be equal. Let the number of diffusing particles per cm^2 on the plane located at x at

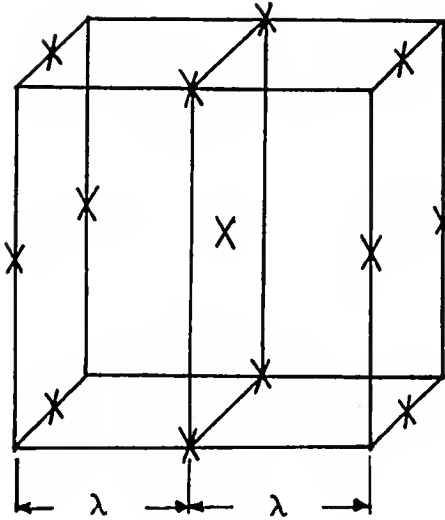


Figure 6. Atomic Plane of Diffusion
in the Metal Lattice

the instant t be represented by $n(x)$. Using Taylor series expansion one therefore gets

$$n(x + \lambda) = n(x) + \left(\frac{\partial n}{\partial x}\right)\lambda + \frac{1}{2}\left(\frac{\partial^2 n}{\partial x^2}\right)\lambda^2 + \dots \quad (42)$$

$$n(x - \lambda) = n(x) - \left(\frac{\partial n}{\partial x}\right)\lambda + \frac{1}{2}\left(\frac{\partial^2 n}{\partial x^2}\right)\lambda^2 + \dots \quad (43)$$

where $n(x + \lambda)$ = the number of hydrogen per cm^2 at plane $x + \lambda$

$n(x - \lambda)$ = the number of hydrogen per cm^2 at plane $x - \lambda$
at time t

The increase of the number of particles located at plane x at instant $t + \delta t$ will be:

$$\delta n(x) = \left[f_r P_r n(x + \lambda) + f_r P_r n(x - \lambda) - 2f_r P_r n(x) \right] \delta t \quad (44)$$

$$\delta n(x) = f_r P_r \delta t \frac{\partial^2 n}{\partial x^2} \lambda^2 \quad (45)$$

from whence we have

$$\frac{\partial n}{\partial t} = f_r P_r \lambda^2 \frac{\partial^2 n}{\partial x^2} \quad (46)$$

Comparing Equation (46) with Fick's second law we see that

$$D = f_r P_r \lambda^2 \quad (47)$$

where D = diffusion coefficient

f_r = a geometric factor and for a f.c.c. lattice is equal to 1/3 when the atomic plane is 001 plane.

The probability P_r is given by (36)

$$P_r = \frac{kT}{h} \frac{Q^\ddagger}{Q^+} \quad (48)$$

where $Q^\ddagger$ = partition function of the activated state

Q^+ = partition function of the normal state.

Further simplification of equation (48) yields

$$P_r = \frac{kT}{h} \left(1 - \exp \frac{-h\nu}{kT} \right) \exp^{-\Delta F^\ddagger/RT} \quad (49)$$

where ν = frequency of vibration of a linear oscillator

$\Delta F^\ddagger$ = free energy of activation.

For the case where $h\nu \ll kT$ Equation (49) reduces to

$$P_r = \nu \exp^{-\Delta F^\ddagger/RT} = \nu \exp^{-\Delta F/RT} \quad (50)$$

and

$$D = f_r \nu \lambda^2 \exp^{-\Delta F/RT} \quad (51)$$

For a face-centered cubic lattice with lattice constant a , and using relationship $\Delta F = \Delta E - T\Delta S$ Equation (51) becomes

$$D = \frac{1}{3} \nu \left(\frac{a}{2}\right)^2 \exp^{\Delta S/R} \exp^{-\Delta E/RT} = \frac{1}{12} \nu a^2 \exp^{\Delta S/R} \exp^{-\Delta E/RT}$$

$$= D_0 \exp^{-\Delta E/RT} \quad (52)$$

where ΔS = entropy of activation

ΔE = energy of activation

$$D_0 = \frac{1}{12} \nu a^2 \exp^{\Delta S/R} \quad (53)$$

Calculating D_0 with estimated values of ΔS , ν and a

$$\nu = 1.75 \times 10^{13} \text{ sec}^{-1}$$

$$a = 3.9 \times 10^{-8} \text{ cm}$$

$$\Delta S = \beta(\Delta E/T_m) = 0.18 \left(\frac{5.600}{2190} \right) = 0.46$$

leads to

$$D_0 = \frac{1.75}{12} \times 10^{13} \times (3.9 \times 10^{-8})^2 \exp^{0.46/1.98} = 1.75 \times 10^{-3} \text{ cm}^2/\text{sec}. \quad (54)$$

If the hydrogen is diffusing normally to 001, 010 or 100 plane, the diffusion constant would be the same; however, if the hydrogen is diffusing normally to 110 plane, the values of f_r and λ would change, indicating that solids are, in general, anisotropic. Initial calculations for diffusion through the 110 plane indicate a higher diffusion coefficient. From these equations it can also be predicted that an expanded lattice, such as a β -phase, would have higher diffusion coefficient provided that no covalent bond is formed between the hydrogen and the palladium atom. The diffusion coefficient in Ag-Pd alloys (34) was found to decrease with increasing silver content. This is

anticipated since silver is a poor hydrogen diffuser. One problem that may arise in the Pd-Ag alloy is the order-disorder phenomenon of Pd and Ag atom in the lattice. As discussed by Krivoglaz and Smirnov (35), the order-disorder of the alloy will affect the value of energy of activation. This is further complicated by the fact that metal crystals are not perfect; therefore, the diffusion would be in different crystallographic planes, which were shown above to possess different diffusion coefficients.

3. Macroscopic Diffusion Equation in Palladium

The macroscopic equation for diffusion of hydrogen in palladium can be written as:

$$\frac{\partial C_A}{\partial t} + \nabla \cdot N_A = R_A \quad (55)$$

where C_A = concentration of A

N_A = molar flux of A

R_A = chemical reaction rate of A

$\nabla \cdot$ = del operator

This can be written in rectangular coordinate as

$$\frac{\partial C_A}{\partial t} + \frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} = R_A \quad (56)$$

$$\text{where } N_{Ax} = \frac{-D \partial C_A}{\partial x} + C_A v^* \quad (57)$$

v^* = molar average velocity

$$= \frac{\sum_i C_i v_i}{\sum_i C_i}$$

In the diffusion of hydrogen through solid, v^* will be near zero, and

since there is no chemical reaction, $R_A = 0$. In this investigation, the flow is in a single direction only, say the x-direction; therefore Equation (56) becomes

$$\frac{\partial C_A}{\partial t} + \frac{\partial N_{Ax}}{\partial x} = 0 \quad (58)$$

but

$$N_{Ax} = \frac{-D \partial C_A}{\partial x} \quad (59)$$

therefore

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D \partial C_A}{\partial x} \right) \quad (60)$$

Assuming the solid to be isotropic

$$\frac{\partial C_A}{\partial t} = \frac{D \partial^2 C_A}{\partial x^2} \quad (61)$$

Let us assume that the upstream surface reaction is very fast so that equilibrium condition prevails between the surface and hydrogen gas. The corresponding boundary conditions and differential equation will be:

$$\text{B.C.1} \quad C = C_1, \quad x = 0, \quad t > 0 \quad (62)$$

$$\text{B.C.2} \quad C = 0, \quad x = L, \quad t > 0 \quad (63)$$

$$\text{B.C.3} \quad C = 0, \quad 0 < x < L, \quad t = 0 \quad (64)$$

$$\frac{\partial C}{\partial t} = \frac{D \partial^2 C}{\partial x^2}, \quad 0 < x < L, \quad t > 0 \quad (65)$$

$$\text{Let } v = C/C_1 \quad (66)$$

then

$$\text{B.C.4} \quad v = 1, \quad x = 0, \quad t > 0 \quad (67)$$

$$\text{B.C.5} \quad v = 0, \quad x = L, \quad t > 0 \quad (68)$$

$$\text{B.C.6} \quad v = 0, \quad 0 < x < L, \quad t = 0 \quad (69)$$

$$\frac{\partial v}{\partial t} = \frac{D \partial^2 v}{\partial x^2} \quad 0 < x < L, \quad t > 0 \quad (70)$$

Taking the Laplace transform of Equation (70) with respect to t

$$sV(x,s) - v(x,0) - \frac{D \partial^2 V(x,s)}{\partial x^2} = 0 \quad (71)$$

where

$$V = \int_0^\infty v \exp^{-st} dt \quad (72)$$

since

$$v(x,0) = 0 \quad (73)$$

Integrating Equation (71)

$$V = C_1 \exp^{+qx} + C_2 \exp^{-qx} \quad (74)$$

where

$$q = \left[\frac{s}{D} \right]^{1/2} \quad (75)$$

Applying B.C. (4) and (5) to eliminate constants C_1 and C_2

$$V = \frac{1}{s(\exp^{qL} - \exp^{-qL})} \left[\exp^{(L-x)q} - \exp^{-(L-x)q} \right] \\ = \frac{\sinh(L-x)q}{s \sinh qL} \quad (76)$$

$$v = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{\exp^{st} \sinh(L-x)q}{s \sinh qL} ds \quad (77)$$

The inverse Laplace transform of Equation (77) with poles of $s = 0$,

and $s = -\frac{Dn^2\pi^2}{L^2}$, $n = 1, 2, 3$ is

$$v = \frac{L-x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \exp^{-\frac{Dn^2\pi^2 t}{L^2}} \sin n\pi \frac{(L-x)}{L} \cos n\pi \\ = \frac{L-x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \exp^{-\frac{Dn^2\pi^2 t}{L^2}} \sin n\pi \frac{(L-x)}{L} \quad (78)$$

The diffusion flux across plane L at any time t will be:

$$N_{x=L} = \left. \frac{-DdC}{dx} \right|_{x=L}$$

$$= \frac{DC_1}{L} + \frac{2DC_1}{L} \sum_{n=1}^{\infty} (-1)^n \exp \frac{-Dn^2 \pi^2 t}{L^2} \quad (79)$$

The diffusion flux at infinite time will be

$$N_{t \rightarrow \infty} = \frac{DC_1}{L} \quad (80)$$

This equation represents the steady-state value of the diffusion flux. Therefore the fraction of the steady-state value reached at time t, SST, will be the ratio between $N_{x=L}$ and $N_{t \rightarrow \infty}$. Thus the value of SST becomes

$$SST = \frac{N_{x=L}}{N_{t \rightarrow \infty}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \frac{-Dn^2 \pi^2 t}{L^2} \quad (81)$$

Letting $\tau = \frac{D\pi^2 t}{L^2}$, the value of SST for different values of τ is plotted in Figure 7.

Figure 8 can be used to find the time to reach 90% of the steady-state value. For example, if $L = 0.01$ cm, $D = 10^{-6}$ cm²/sec., the time t to reach 90% of equilibrium value will be (with $\tau = 3$ when $SST = 0.90$ from Figure 7):

$$\tau = 3 = \frac{(10^{-6})(3.14)^2 t}{(0.01)^2} \quad (82)$$

and

$$t = 30 \text{ secs.}$$

In the case where there is a surface effect, the equation will be of the form

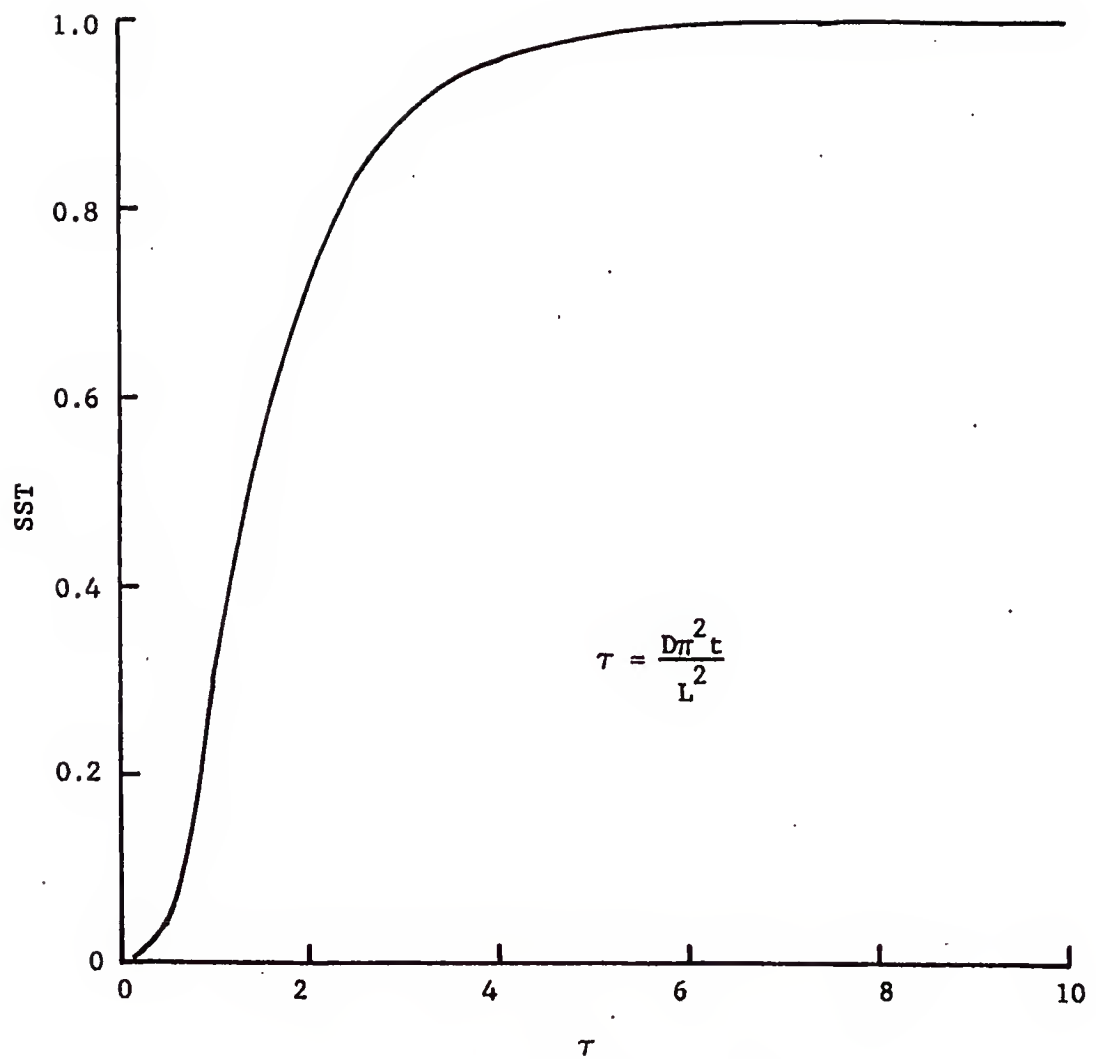


Figure 7. Value of SST for different τ

$$\text{B.C.7} \quad \frac{\partial C}{\partial x} = \frac{k'_G}{G}(C - C_1) = k_G(C - C_1), \quad x = 0, \quad t > 0 \quad (83)$$

$$\text{B.C.8} \quad C = 0, \quad x = L, \quad t > 0 \quad (84)$$

$$\text{B.C.9} \quad C = 0, \quad 0 < x < L, \quad t = 0 \quad (85)$$

$$\frac{\partial C}{\partial t} = \frac{D \partial^2 v}{\partial x^2}, \quad 0 < x < L, \quad t > 0 \quad (86)$$

Using Equation (66) the Laplace transform will be

$$v = C_1 \exp^{qx} + C_2 \exp^{-qx} \quad (87)$$

where

$$q = \left[\frac{s}{D} \right]^{1/2} \quad (88)$$

Applying the boundary conditions to eliminate C_1 and C_2 we obtain

$$v = \frac{k_G L \sinh(L-x)q}{s(qL \cosh qL + k_G L \sinh qL)} \quad (89)$$

The inverse Laplace transform is

$$v = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \frac{k_G L \exp^{st} \sinh(L-x)q ds}{s(qL \cosh qL + k_G L \sinh qL)} \quad (90)$$

The poles are $s = 0$, and $s = \frac{-D\xi^2}{L^2}$ where ξ are the roots of the transcendental equation

$$\tan \xi = \frac{-\xi}{k_G L} \quad (91)$$

Solution of Equation (90) by residue method results in

$$v = \frac{k_G(L-x)}{1+k_G L} + 2(k_G L)^2 \sum_{n=0}^{\infty} \frac{\exp \frac{-D\xi_n^2 t}{L^2} \sin \frac{(L-x)\xi_n}{L}}{\xi_n \cos \xi_n (\xi_n^2 + (k_G L)^2 + k_G L)} \quad (92)$$

Now $N_{x=L} = \frac{-DC_1 dv}{dx}$

$$= \frac{k_G DC_1}{1 + k_G L} + \frac{2D(k_G L)^2 C_1}{L} \sum_{n=0}^{\infty} \frac{\exp^{-D\xi_n^2 t}}{[\cos \xi_n] [\xi_n^2 + (k_G L)^2 + k_G L]} \quad (93)$$

Using relationship $\tan \xi_n = \frac{-\xi_n}{k_G L}$ (94)

$$\cos \xi_n = (-1)^n \frac{k_G L}{\{\xi_n^2 + (k_G L)^2\}^{1/2}} \quad (95)$$

$$N_{x=L} = \frac{k_G DC_1}{1 + k_G L} + 2Dk_G C_1 \sum_{n=1}^{\infty} \frac{(-1)^n \{\xi_n^2 + (k_G L)^2\}^{1/2} \exp \frac{-D\xi_n^2 t}{L^2}}{\xi_n^2 + (k_G L)^2 + k_G L} \quad (96)$$

$$N_{t \rightarrow \infty} = \frac{k_G DC_1}{1 + k_G L} = \frac{DC_1}{L} \left(\frac{k_G}{\frac{1}{L} + k_G} \right) \quad (97)$$

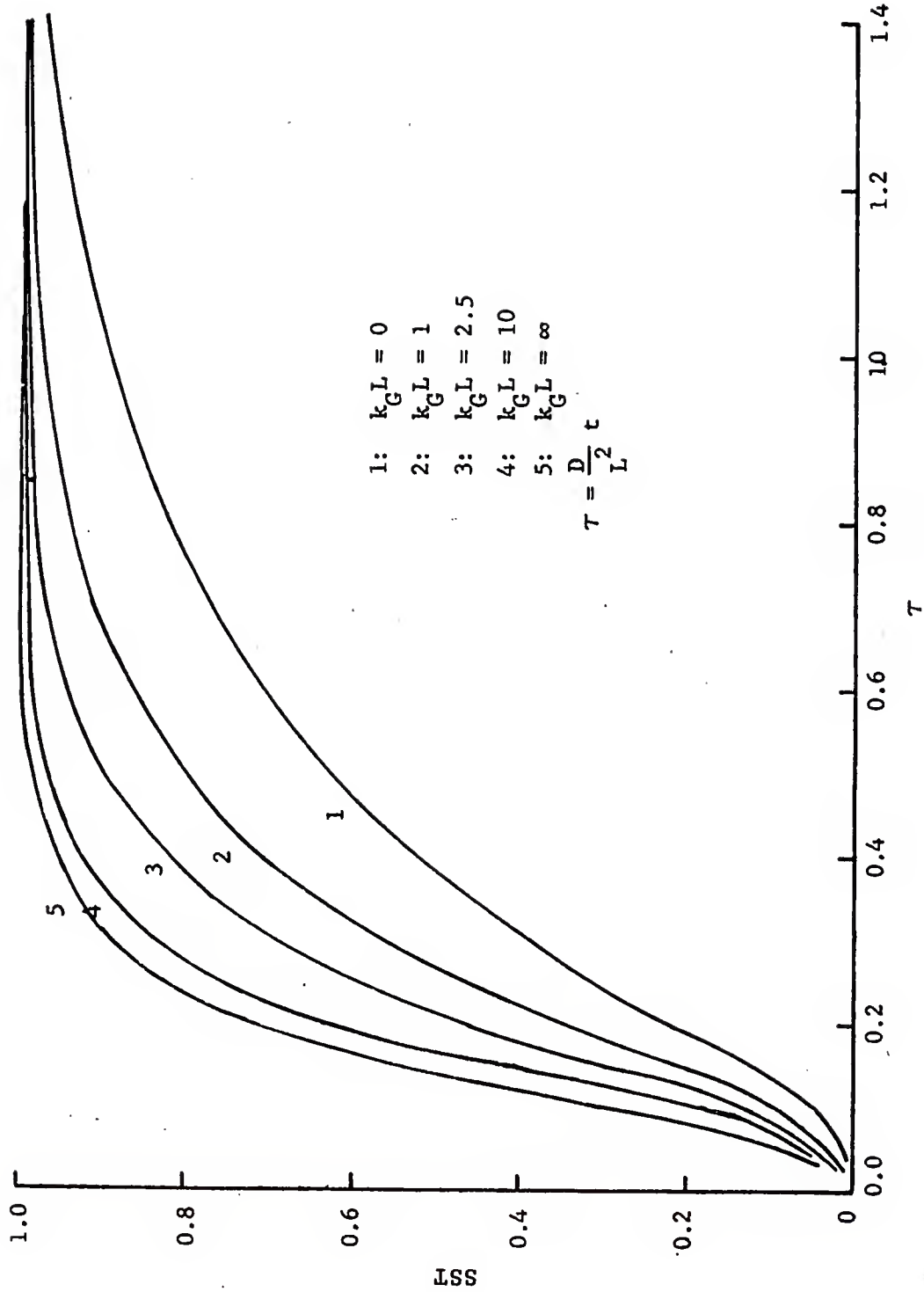
$$\lim_{\substack{t \rightarrow \infty \\ k_G \rightarrow \infty}} N_{x=L} = \frac{DC_1}{L} \quad (98)$$

Equation (98) is similar to Equation (80).

Equation (96) can be used to ascertain the time required to reach steady-state by using the parameter $\tau = \frac{Dt}{L^2}$ and $k_G L$, thus by the previous method

$$SST = \frac{N_{x=L}}{N_{t \rightarrow \infty}} = 1 + 2(1 + k_G L) \sum_{n=1}^{\infty} \frac{(-1)^n \{\xi_n^2 + (k_G L)^2\}^{1/2} \exp \frac{-D\xi_n^2 t}{L^2}}{\xi_n^2 + (k_G L)^2 + k_G L} \quad (99)$$

The value of SST for different values of τ and $k_G L$ are shown in Figure 8.

Figure 8. Value of SST for Different τ

CHAPTER III

EXPERIMENTAL PROCEDURE

A. Experimental Apparatus

The experimental apparatus consisted of a diffusion cell, pressure measuring system, vacuum system, gas cylinders and a temperature control system. These are shown in Figure 9.

The diffusion cells, shown in detail in Figures 10 and 11, consisted of a stainless steel flange, a Pd-Ag membrane, and copper gasket held together by four bolts. The silver-palladium membranes, 1 1/8 inches in diameter, were punched from 25% silver-palladium foil. A cavity 1/2 inches in diameter and 1/16 inches deep was machined in the upstream flange to serve as a gas chamber; a gas inlet and outlet to this chamber were also provided as shown. The downstream flange was similar except that only a gas outlet was provided; however, a thermocouple well was machined in the downstream flange. The downstream cavity was connected to a stainless steel (5641 cm³) tank which provided enough capacity to prevent the downstream pressure from changing too rapidly during measurement.

A thermocouple gauge was used to measure the vacuum on the downstream side from 1-1000 microns. A Mcleod gauge was used to measure the pressure change in the downstream side of the apparatus during the diffusion experiment. A pressure regulator was used to provide the desired pressure from the feed gas cylinder, an extra pressure gauge is also included in the line.

The temperature control system consists of a temperature recorder-controller and a tube furnace. A chromel-alumel thermocouple

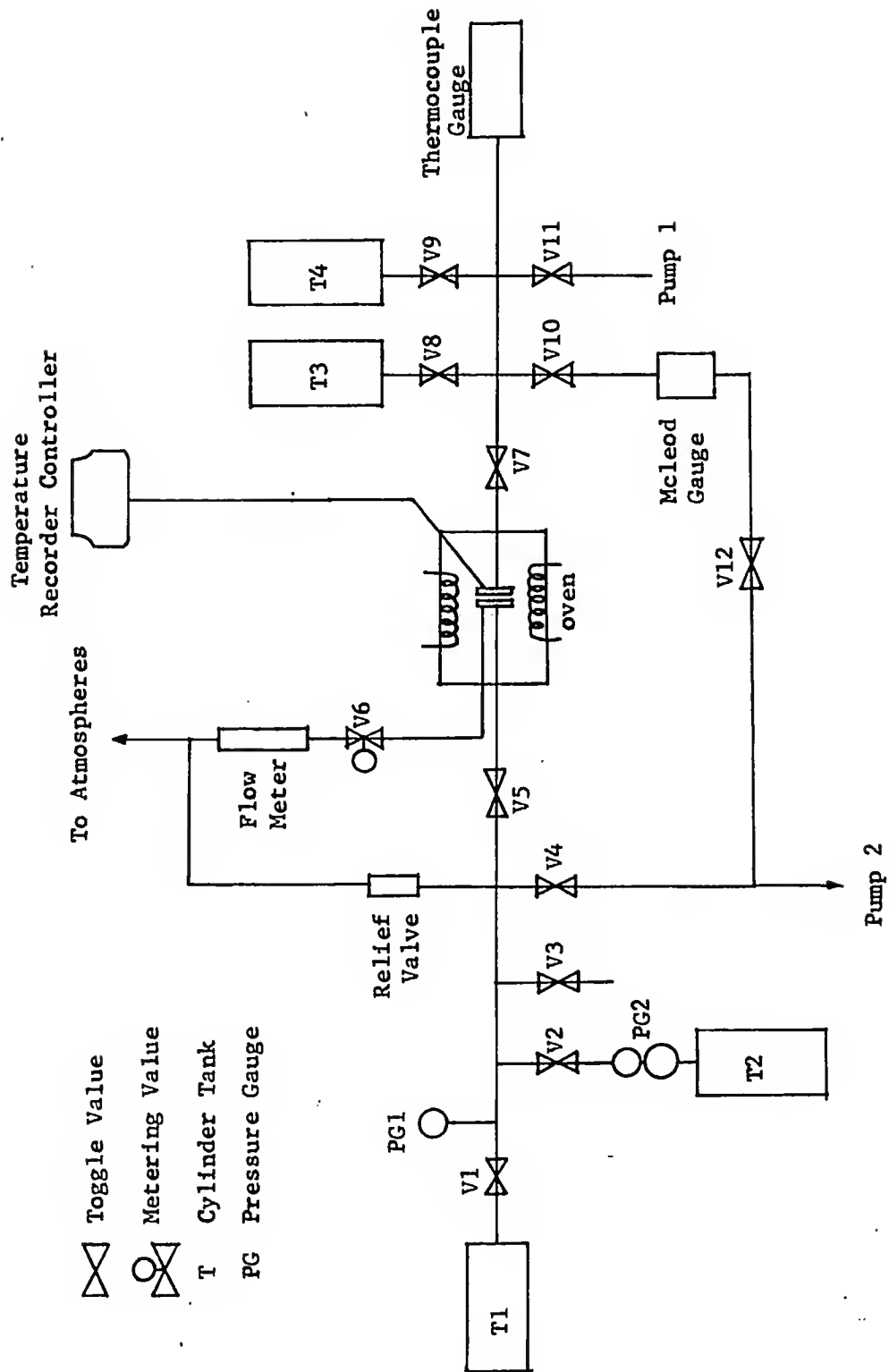


Figure 9. Apparatus for Measuring Transport Rate of Hydrogen Through Palladium

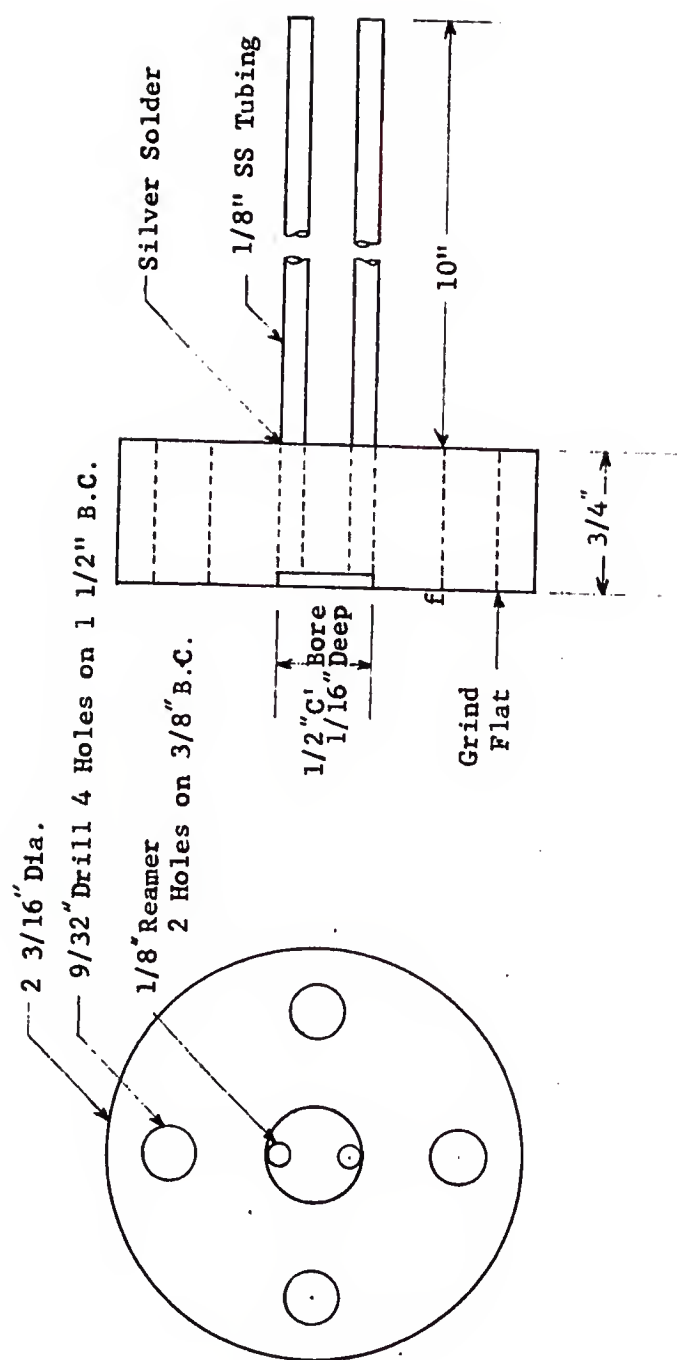


Figure 10. Diffusion Cell Upstream Flange

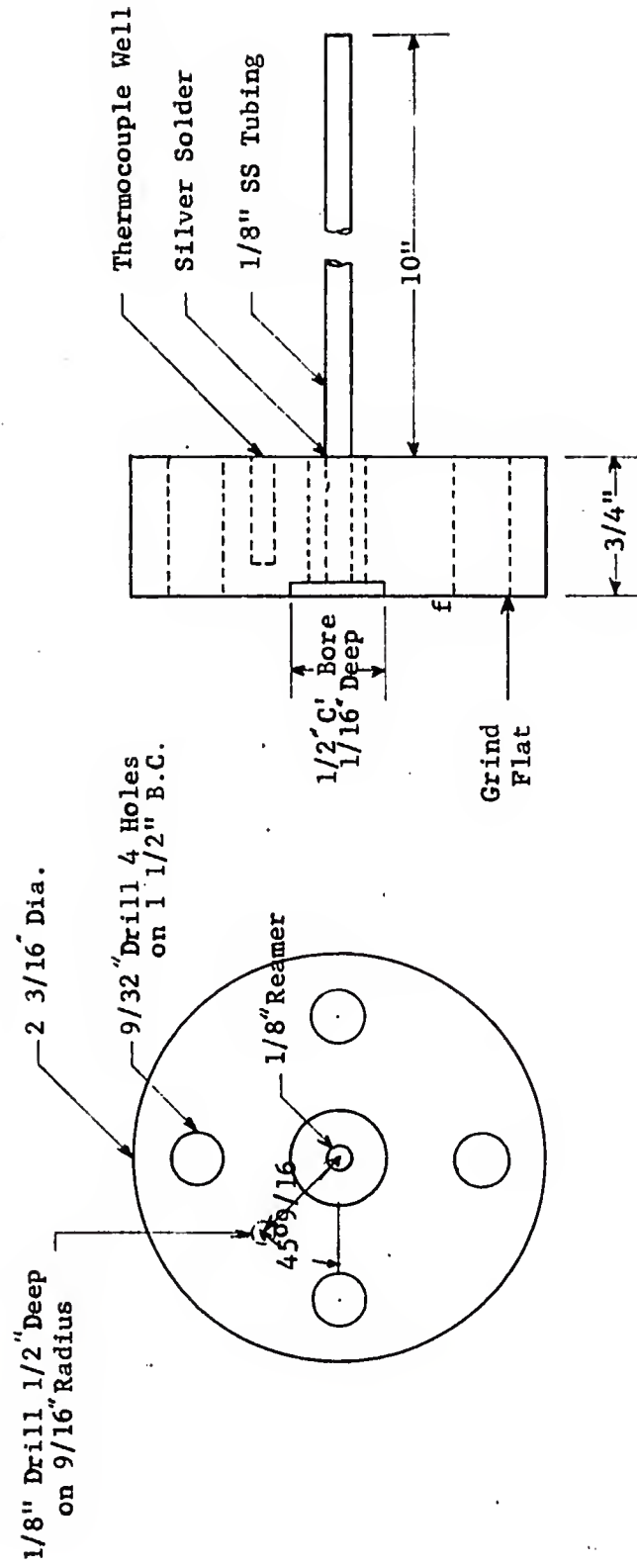


Figure 11. Diffusion Cell Downstream Flange

was used to measure the temperature of the membrane.

The flow through the system was controlled by a toggle valve, and a flowmeter was incorporated in the upstream side to regulate the bleed rate. A rupture diaphragm with a bursting pressure of 50 psig was installed on the upstream side.

Two Welch vacuum pumps were used for evacuating the system. Small gas cylinders were used for storage of feed gas and for the diffused hydrogen gas. The temperature recorder has an estimated error of $\pm 1^{\circ}\text{C}$ and the Mcleod gauge has an estimated error of ± 0.05 mm in the range of pressure used.

B. Experimental Procedure

The transport rate of hydrogen through the palladium-silver membrane was measured by trapping the diffused hydrogen gas in the downstream side for a short length of time and determining the pressure change during this time interval.

The experimental procedure is important because a different procedure will give different results. In all these experiments, unless otherwise specified, the first set of experiments is always disregarded, because the palladium-silver membrane gave a lower transport rate when used for the first time. The transport rate was found to increase after one cycle and it also became more reproducible.

Two experimental procedures were used to determine the transport rate: Procedure A altered the pressure while keeping the temperature constant. In Procedure B the temperature was altered while keeping the pressure constant. In both procedures, the pressure and temperature was always increased from a lower value to a higher one.

Altering this sequence was found to produce different results. A more detailed description of these procedures is given in Appendix B.

CHAPTER IV

EXPERIMENTAL RESULTS AND CALCULATIONS

A. Experimental Evaluation of the Transport Rate Per Unit Area

The transport rate of hydrogen per unit area through 0.106 mm 25% palladium-silver foil were calculated from the pressure change and time data. The experimental data from these runs are tabulated in Tables 1-19. The membrane area for all these runs was 1.268 cm².

Hydrogen is admitted to the upstream side and the downstream pressure increases from P_i to P_f at an interval time ϕ . The moles of hydrogen diffusing, assuming ideal gas behavior, will be:

$$n_2 - n_1 = \frac{V_c (P_f - P_i)}{RT} \quad (100)$$

where n_1 = gm. moles at the start of the experiment

n_2 = gm. moles at time ϕ

P_i = downstream pressure at start of the experiment in mm Hg

P_f = downstream pressure at time ϕ in mm Hg

V_c = volume of the downstream compartment in Cm³

T = absolute temperature °K

R = gas constant

The transport rate per unit area will be given by:

$$N_A = \frac{n_2 - n_1}{A\phi} = \frac{V_c \Delta P}{A\phi RT} \quad (101)$$

where N_A = transport rate per unit area in gm.moles/cm² sec.

V_c = volume of downstream compartment, 5641 cm³

A = area, 1.268 cm²

ϕ = time, secs.

TABLE 1

THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Bleed Rate B: 3.79×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec
			P_i	P_f		Membrane	Gas	
1	A	1069	2.0	13.0	350	300	29.5	7.41
		1380	2.2	15.2	350	300	29.5	8.75
		1690	2.4	17.2	350	300	30.0	9.95
		2000	2.6	18.7	350	300	30.0	10.84
		2310	2.7	20.7	350	300	30.0	12.09
1	A	1069	2.2	14.3	350	340	30.0	8.16
		1380	2.4	16.7	350	340	30.0	9.62
		1690	2.6	18.7	350	340	29.0	10.89
		2000	2.8	20.3	350	340	29.0	11.83
		2310	2.9	22.4	350	340	28.5	13.21
1	A	1069	2.2	15.3	350	380	27.8	8.88
		1380	2.4	17.6	350	380	27.5	9.64
		1690	2.6	19.6	350	380	27.5	11.51
		2000	2.8	21.4	350	380	27.5	12.58
		2310	3.0	23.4	350	380	27.0	13.83
1	A	1069	2.4	15.9	350	420	27.0	9.17
		1380	2.6	18.4	350	420	27.0	10.71
		1690	2.8	20.7	350	420	27.0	12.14
		2000	3.0	22.5	350	420	26.8	13.25
		2310	3.1	24.3	350	420	26.5	14.46

TABLE 1 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec
			P_i	P_f		Membrane	Gas	
1	A	1069	2.4	17.0	350	460	26.5	9.91
		1380	2.6	19.5	350	460	26.5	11.51
		1690	2.8	21.9	350	460	26.5	12.98
		2000	3.0	23.6	350	460	26.5	14.01
		2310	3.2	22.8	300	460	26.0	15.62

TABLE 2

THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Expt. No.	Procedure	Bleed Rate B: 3.79×10^{-5} gm.moles/cm ² sec										$N_A \times 10^6$ gm.moles/cm ² sec
		Pressure mm Hg		Pressure, mm Hg		Time Secs	Temp. °C					
		P_i	P_f	P_i	P_f		Membrane	Gas				
2	B	1069	2.0	12.4	350	300	27.0				7.05	
		1069	2.2	13.9	350	340	28.5				7.94	
		1069	2.3	15.1	350	380	29.5				8.66	
		1069	2.4	16.0	350	420	29.5				9.15	
		1069	2.5	16.9	350	460	29.0				9.73	
2	B	1380	2.2	14.4	350	300	27.0				8.30	
		1380	2.4	16.1	350	340	27.5				9.28	
		1380	2.5	17.5	350	380	27.5				10.22	
		1380	2.6	18.4	350	420	27.0				10.71	
		1380	2.7	19.4	350	460	26.5				11.38	

TABLE 2 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec
			P_i	P_f		Membrane	Gas	
2	B	1690	2.4	16.7	350	300	27.0	9.68
		1690	2.6	18.2	350	340	28.5	10.53
		1690	2.6	19.4	350	380	29.0	11.29
		1690	2.8	20.4	350	420	28.0	11.91
		1690	2.9	21.5	350	460	28.0	12.58
2	B	2000	2.6	18.3	350	300	28.5	10.62
		2000	2.8	21.8	381	340	29.7	11.69
		2000	2.9	21.5	350	380	28.5	12.58
		2000	3.0	22.7	350	420	28.0	13.30
		2000	3.1	23.8	350	460	27.5	14.06
2	B	2310	2.8	22.0	366	300	27.5	12.45
		2310	3.0	22.6	350	340	29.0	13.21
		2310	3.0	24.0	350	380	29.0	14.14
		2310	3.2	25.2	350	420	29.0	14.90
		2310	3.3	23.2	300	460	28.0	15.71

TABLE 3
EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 30% CH ₄ , 10% N ₂ , 60% H ₂										
Bleed Rate B: 0.55×10^{-5} gm.moles/cm ² sec										
Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		N _A × 10 ⁶ gm.moles/cm ² sec		B/N _A
			P _i	P _f		Membrane	Gas			
3	A	1069	0.0	4.5	350	300	30.5	3.02		1.82
		1380	1.4	6.9	350	300	30.5	3.69		1.50
		1690	1.6	7.7	350	300	31.0	4.08		1.35
		2000	1.6	7.8	350	300	31.5	4.14		1.23
		2310	1.6	8.7	350	300	31.0	4.75		1.16
3	A	1069	1.5	7.9	350	340	31.5	4.28		1.29
		1380	1.7	9.8	350	340	30.5	5.44		1.01
		1690	1.8	10.2	350	340	30.5	5.62		0.98
		2000	1.9	10.8	350	340	29.0	6.00		0.92
		2310	2.0	12.0	350	340	29.0	6.74		0.82
3	A	1069	1.8	10.2	350	380	29.0	5.67		0.97
		1380	1.9	11.4	350	380	28.5	6.40		0.86
		1690	2.0	12.3	350	380	28.5	6.96		0.79
		2000	2.0	12.0	350	380	28.0	6.78		0.81
		2310	2.1	13.0	350	380	28.0	7.38		0.75

TABLE 3 (Continued)

Expt. No.	Procedure	Pressure mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec	B/N A
		P_i	P_f		Membrane	Gas		
3	A	1069	1.8	10.8	350	420	27.0	0.90
		1380	2.0	12.0	350	420	27.0	0.81
		1690	2.0	11.6	350	420	27.0	0.85
		2000	2.0	12.4	350	420	27.0	0.78
		2310	2.2	13.6	350	420	26.5	0.71
3	A	1069	1.9	11.0	350	460	26.5	0.89
		1380	2.0	12.3	350	460	26.5	0.78
		1690	2.1	12.4	350	460	26.5	0.78
		2000	2.1	12.6	350	460	26.5	0.77
		2310	2.2	13.6	350	460	26.0	0.71

TABLE 4

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANEFeed Gas Composition: 30% CH₄, 10% N₂, 60% H₂Bleed Rate B: 1.08×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec	B/N A
		P_i	P_f		Membrane	Gas		
4	A	1069	1.4	6.2	350	300	28.0	3.42
		1380	1.5	7.5	350	300	29.0	2.66
		1690	1.6	8.4	350	300	29.0	2.35
		2000	1.7	8.9	350	300	29.5	2.22
		2310	1.8	9.8	350	300	29.0	1.99

TABLE 4 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm. moles/cm ² sec.	B/N _A
			P _i	P _f		Membrane	Gas		
4	A	1069	1.6	8.6	350	340	27.0	4.76	2.26
		1380	1.8	10.2	350	340	27.0	5.70	1.89
		1690	1.9	11.2	350	340	26.5	6.34	1.70
		2000	1.9	11.9	350	340	26.0	6.80	1.58
		2310	2.0	12.4	353	340	26.0	7.36	1.46
4	A	1069	1.8	9.9	350	380	26.0	5.53	1.95
		1380	1.9	11.5	350	380	26.0	6.54	1.65
		1690	2.0	11.8	352	380	25.5	7.01	1.54
		2000	2.0	12.9	350	380	25.5	7.45	1.45
		2310	2.2	13.9	350	380	25.5	7.99	1.35
4	A	1069	1.8	10.8	350	420	25.5	6.14	1.76
		1380	2.0	12.4	350	420	26.0	7.10	1.52
		1690	2.0	13.0	350	420	25.5	7.50	1.44
		2000	2.1	13.5	350	420	25.5	7.79	1.38
		2310	2.2	14.5	350	420	25.5	8.39	1.28
4	A	1069	1.9	11.4	350	460	25.0	6.49	1.66
		1380	2.0	12.9	350	460	25.0	7.45	1.45
		1690	2.1	13.9	350	460	25.0	8.08	1.33
		2000	2.2	14.1	350	460	25.0	8.12	1.33
		2310	2.3	15.1	350	460	25.0	8.75	1.23

TABLE 5

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Bleed Rate B: 1.88×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec	B/N A
			P _i	P _f		Membrane	Gas		
5	A	1069	0.0	5.5	350	300	27.0	3.73	5.04
		1380	1.6	8.1	371	300	27.0	4.17	4.50
		1690	1.6	8.8	350	300	27.5	4.87	3.86
		2000	1.8	10.0	350	300	28.0	5.56	3.38
		2310	1.8	10.7	350	300	28.5	6.02	3.12
5	A	1069	1.6	8.8	350	340	29.0	4.86	3.87
		1380	1.8	10.4	354	340	29.8	5.98	3.14
		1690	2.0	12.0	350	340	29.5	6.74	2.79
		2000	2.0	12.9	350	340	29.5	7.34	2.54
		2310	2.1	13.6	350	340	28.8	7.76	2.42
5	A	1069	1.8	10.4	350	380	28.0	5.82	3.10
		1380	2.0	11.8	350	380	27.5	6.65	2.70
		1690	2.0	12.4	350	380	27.0	7.05	2.56
		2000	2.2	13.6	350	380	27.5	7.72	2.33
		2310	2.2	14.5	350	380	27.0	8.34	2.16
5	A	1069	1.8	11.0	350	420	27.0	6.25	3.00
		1380	2.0	12.5	350	420	27.0	7.14	2.64
		1690	2.1	13.5	350	420	27.0	7.74	2.43
		2000	2.2	14.2	350	420	26.5	8.17	2.30
		2310	2.3	15.3	350	420	26.5	8.84	2.12

TABLE 5 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec	B/N A
			P_i	P_f		Membrane	Gas		
5	A	1069	1.9	11.8	350	460	26.5	6.74	2.80
		1380	2.0	13.1	350	460	26.5	7.54	2.50
		1690	2.2	14.1	350	460	26.5	8.09	2.32
		2000	2.3	15.0	350	460	26.5	8.61	2.18
		2310	2.4	16.2	350	460	26.5	9.36	2.00

TABLE 6

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Bleed Rate B: 2.80×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec	B/N A
			P_i	P_f		Membrane	Gas		
6	A	1069	0.0	5.9	350	300	28.5	3.99	7.01
		1380	1.6	8.6	350	300	29.0	4.73	5.91
		1690	1.7	9.7	350	300	29.0	5.40	5.20
		2000	1.8	10.4	350	300	30.0	5.78	4.85
		2310	1.8	11.4	350	300	30.0	6.45	4.35
6	A	1069	1.7	9.1	350	340	30.0	4.97	5.64
		1380	1.8	10.8	350	340	30.0	6.07	4.61
		1690	2.0	11.8	350	340	30.5	6.58	4.26
		2000	2.0	10.7	350	340	30.0	7.18	3.90
		2310	2.2	11.7	350	340	29.5	7.87	3.56

TABLE 6 (Continued)

Expt. No.	Procedure	Pressure mm Hg		Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
		P_i		P_f			Membrane	Gas		
6	A	1069	1.8	10.4		350	380	29.0	5.80	4.83
		1380	2.0	12.1		350	380	29.0	6.83	4.10
		1690	2.1	12.3		350	380	28.5	7.56	3.70
		2000	2.2	13.9		350	380	28.0	7.94	3.53
		2310	2.2	14.9		350	380	28.0	8.61	3.25
6	A	1069	1.9	12.2		350	420	27.5	6.98	4.00
		1380	2.0	12.9		350	420	28.0	7.36	3.80
		1690	2.2	13.9		354	420	29.5	7.90	3.54
		2000	2.2	14.7		350	420	30.0	8.41	3.32
		2310	2.4	15.8		350	420	30.5	9.01	3.11
6	A	1069	2.0	12.0		350	460	31.0	6.69	4.20
		1380	2.1	13.3		350	460	30.5	7.85	3.56
		1690	2.2	14.8		350	460	30.0	8.48	3.30
		2000	2.3	15.5		350	460	30.5	8.86	3.16
		2310	2.4	16.8		350	460	30.5	9.75	2.86

TABLE 7

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Bleed Rate B: 0.38×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P ₁	P ₂		Membrane	Gas		
7	A	1069	0.0	7.8	350	300	28.5	5.47	0.70
		1380	1.9	11.2	350	300	28.5	6.29	0.61
		1690	1.9	11.4	350	300	29.0	6.40	0.60
		2000	2.0	13.0	350	300	29.0	7.41	0.52
		2310	2.2	14.0	350	300	29.0	7.94	0.48
7	A	1069	1.9	10.8	350	340	29.5	5.98	0.64
		1380	2.0	11.9	350	340	29.8	6.67	0.57
		1690	2.0	12.9	350	340	30.0	7.32	0.52
		2000	2.2	14.3	350	340	30.0	8.12	0.47
		2310	2.3	15.3	350	340	29.5	8.75	0.44
7	A	1069	2.0	11.8	350	380	29.0	6.60	0.58
		1380	2.0	12.6	350	380	28.5	7.16	0.50
		1690	2.1	13.5	350	380	28.5	7.36	0.52
		2000	2.2	14.9	350	380	28.0	8.59	0.45
		2310	2.3	16.1	350	380	28.0	9.28	0.41
7	A	1069	2.0	12.4	350	420	27.0	7.05	0.54
		1380	2.1	13.5	350	420	27.0	7.74	0.50
		1690	2.2	14.3	350	420	27.0	8.21	0.47
		2000	2.3	15.6	350	420	27.0	9.04	0.42
		2310	2.4	17.2	350	420	27.0	10.00	0.38

TABLE 7 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P_i	P_f		Membrane	Gas		
7	A	1069	2.2	13.0	350	460	27.0	7.32	0.52
		1380	2.2	13.5	350	460	26.5	7.67	0.50
		1690	2.3	14.7	350	460	26.5	8.43	0.45
		2000	2.4	17.0	366	460	26.0	9.50	0.40
		2310	2.5	18.0	350	460	26.0	10.57	0.36

TABLE 8

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Bleed Rate B: 0.52×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P_i	P_f		Membrane	Gas		
8	A	1069	0.0	7.9	350	300	27.8	5.35	0.98
		1380	2.0	12.1	400	300	28.0	6.20	0.84
		1690	2.0	11.7	350	300	28.0	6.49	0.81
		2000	2.2	13.5	350	300	28.5	7.58	0.69
		2310	2.2	14.3	350	300	29.0	8.16	0.64
8	A	1069	2.0	11.6	350	340	28.5	6.49	0.81
		1380	2.1	13.1	350	340	29.5	7.41	0.71
		1690	2.2	14.1	350	340	29.0	8.03	0.65
		2000	2.2	14.9	350	340	29.0	8.57	0.61
		2310	2.4	16.2	350	340	28.5	9.33	0.56

TABLE 8 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm. moles/cm ² sec.	B/N _A
			P_i	P_f		Membrane	Gas		
8	A	1069	2.0	12.0	350	380	27.0	6.78	0.77
		1380	2.1	13.3	352	380	27.5	7.58	0.69
		1690	2.2	14.4	350	380	27.0	8.30	0.63
		2000	2.3	15.7	350	380	27.0	9.10	0.57
		2310	2.4	17.0	350	380	27.0	9.91	0.53
8	A	1069	2.0	12.9	350	420	27.0	7.41	0.71
		1380	2.1	14.3	350	420	27.0	8.30	0.63
		1690	2.2	15.0	350	420	27.0	8.70	0.60
		2000	2.5	16.3	350	420	27.0	9.46	0.55
		2310	2.5	17.6	350	420	27.0	10.26	0.51
8	A	1069	2.0	13.5	350	460	27.0	7.81	0.67
		1380	2.3	15.3	350	460	26.5	8.83	0.59
		1690	2.4	15.7	350	460	26.0	9.06	0.58
		2000	2.5	17.1	350	460	26.0	9.95	0.53
		2310	2.6	18.9	350	460	26.0	11.11	0.47

TABLE 9

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂
Bleed Rate B: 1.11×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P _i	P _f		Membrane	Gas		
9	A	1069	0.0	7.5	350	300	28.0	5.09	2.18
		1380	1.9	11.0	350	300	28.5	6.16	1.80
		1690	2.0	12.6	350	300	29.5	7.18	1.55
		2000	2.1	13.7	350	300	30.0	7.81	1.42
		2310	2.2	15.2	350	300	29.0	8.75	1.27
9	A	1069	1.9	11.7	350	340	29.0	6.60	1.68
		1380	2.0	13.2	350	340	28.5	7.58	1.46
		1690	2.2	14.5	350	340	28.5	8.30	1.33
		2000	2.3	14.5	350	340	28.0	8.92	1.24
		2310	2.4	16.6	350	340	27.5	9.64	1.15
9	A	1069	2.0	12.4	350	380	27.0	7.05	1.57
		1380	2.2	13.9	350	380	27.0	7.94	1.40
		1690	2.2	15.2	350	380	27.0	8.83	1.34
		2000	2.4	16.3	350	380	27.0	9.44	1.18
		2310	2.5	17.8	350	380	26.5	10.40	1.07
9	A	1069	2.0	13.3	350	420	26.5	7.67	1.45
		1380	2.2	14.9	350	420	26.0	8.66	1.28
		1690	2.4	16.6	350	420	26.0	9.68	1.15
		2000	2.5	17.4	350	420	26.0	10.11	1.10
		2310	2.6	18.7	350	420	26.0	10.98	1.01

TABLE 9 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N A
			P_i	P_f		Membrane	Gas		
9	A	1069	2.1	13.7	350	460	26.0	7.90	1.40
		1380	2.4	15.5	350	460	26.0	8.92	1.24
		1690	2.5	16.8	350	460	26.0	9.73	1.14
		2000	2.6	18.0	350	460	26.0	10.49	1.06
		2310	2.7	19.6	350	460	26.0	11.51	0.96

TABLE 10

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Bleed Rate B: 2.95×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N A
			P_i	P_f		Membrane	Gas		
10	A	1069	0.0	8.3	350	300	27.0	5.62	5.25
		1380	1.9	11.4	350	300	27.0	6.45	4.58
		1690	2.0	12.6	350	300	27.0	7.18	4.11
		2000	2.1	13.9	350	300	27.5	7.99	3.69
		2310	2.2	15.3	350	300	27.5	8.88	3.32
10	A	1069	2.0	12.6	388	340	27.5	7.18	4.11
		1380	2.1	13.1	350	340	27.5	7.81	3.78
		1690	2.2	14.9	350	340	27.5	8.61	3.43
		2000	2.3	16.3	350	340	27.5	9.50	3.10
		2310	2.4	17.8	350	340	27.0	10.44	2.82

TABLE 10 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm. moles/cm ² sec.	B/N A
			P_i	P_f		Membrane	Gas		
10	A	1069	2.0	13.0	350	380	26.0	7.50	3.93
		1380	2.2	14.6	350	380	26.0	8.43	3.50
		1690	2.3	16.2	350	380	26.0	9.46	3.12
		2000	2.4	17.4	350	380	26.0	10.22	2.88
		2310	2.6	18.9	350	380	25.5	11.15	2.64
10	A	1069	2.1	13.7	350	420	25.0	7.94	3.72
		1380	2.2	15.5	350	420	25.5	9.08	3.25
		1690	2.4	16.8	350	420	25.5	9.82	3.00
		2000	2.5	18.2	350	420	25.5	10.71	2.74
		2310	2.6	19.7	350	420	25.5	11.70	2.52
10	A	1069	2.2	14.1	350	460	25.7	8.12	3.64
		1380	2.4	16.3	350	460	25.5	9.50	3.10
		1690	2.6	17.6	350	460	25.5	10.26	2.98
		2000	2.6	19.2	350	460	25.5	11.33	2.60
		2310	2.8	20.8	350	460	25.5	12.31	2.40

TABLE 11

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 25.6% N ₂ , 74.4% H ₂									
Bleed Rate B: 0.93 x 10 ⁻⁵ gm.moles/cm ² sec									
Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		N _A x 10 ⁶ gm.moles/cm ² sec.	B/N A
			P _i	P _f		Membrane	Gas		
11	A	1069	1.6	9.1	350	300	27.0	5.09	1.82
		1380	2.0	11.0	350	300	27.0	6.11	1.51
		1690	2.0	12.0	350	300	27.0	6.78	1.37
		2000	2.2	12.9	350	300	27.0	7.27	1.27
		2310	2.2	14.1	350	300	27.0	8.08	1.15
11	A	1069	1.9	11.1	350	340	27.0	6.25	1.48
		1380	2.0	12.6	350	340	27.0	7.18	1.29
		1690	2.1	13.3	350	340	27.0	7.58	1.22
		2000	2.2	14.1	350	340	27.0	8.08	1.14
		2310	2.3	15.5	350	340	27.0	8.97	1.03
11	A	1069	2.0	11.6	350	380	27.0	6.51	1.42
		1380	2.1	13.3	350	380	27.0	7.63	1.21
		1690	2.2	14.0	350	380	27.0	8.16	1.13
		2000	2.2	15.0	350	380	27.0	8.70	1.06
		2310	2.4	16.2	350	380	27.0	9.37	0.99
11	A	1069	2.0	12.4	350	420	26.5	7.05	1.31
		1380	2.1	13.9	350	420	26.5	8.03	1.15
		1690	2.2	14.8	350	420	26.5	8.57	1.08
		2000	2.3	15.8	350	420	26.5	9.19	1.01
		2310	2.4	17.0	350	420	26.5	9.91	0.93

Feed Gas Composition: 25.6% N₂, 74.4% H₂Bleed Rate B: 0.93×10^{-5} gm. moles/cm sec

TABLE 11 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm sec.	B/N A
			P_i	P_f		Membrane	Gas		
11	A	1069	2.1	13.0	350	460	26.0	7.41	1.25
		1380	2.2	14.6	350	460	26.0	8.39	1.10
		1690	2.3	15.3	350	460	26.0	8.88	1.04
		2000	2.4	16.6	350	460	26.0	9.68	0.96
		2310	2.6	18.0	350	460	26.0	10.49	0.88

TABLE 12

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 25.6% N_2 , 74.4% H_2

Bleed Rate B: 2.46×10^{-5} gm.moles/cm sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm sec.	B/N A
			P_i	P_f		Membrane	Gas		
12	A	1069	1.6	9.0	350	300	25.0	5.04	4.90
		1380	1.8	10.5	350	300	25.0	5.96	4.13
		1690	1.9	11.6	350	300	24.5	6.65	3.70
		2000	2.1	12.9	350	300	24.5	7.38	3.34
		2310	2.2	14.1	350	300	24.5	8.16	3.02
12	A	1069	1.9	10.8	350	340	24.0	6.11	4.03
		1380	2.0	12.4	350	340	23.5	7.14	3.46
		1690	2.1	13.5	350	340	23.5	7.85	3.14
		2000	2.2	14.7	350	340	23.0	8.61	2.86
		2310	2.4	15.8	350	340	23.0	9.19	2.68

TABLE 12 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm sec.	B/N
			P_i	P_f		Membrane	Gas		
12	A	1069	2.0	11.6	350	380	22.0	6.63	3.72
		1380	2.1	13.3	350	380	22.0	7.72	3.19
		1690	2.2	14.5	350	380	22.0	8.52	2.89
		2000	2.3	15.7	350	380	22.0	9.17	2.69
		2310	2.5	17.2	350	380	22.0	10.17	2.42
12	A	1069	2.0	12.5	350	420	21.0	7.27	3.39
		1380	2.2	14.4	350	420	21.0	8.46	2.92
		1690	2.3	15.3	350	420	21.0	9.01	2.74
		2000	2.4	16.5	350	420	23.2	9.73	2.54
		2310	2.5	18.0	350	420	22.0	10.71	2.30
12	A	1069	2.2	13.3	350	460	21.0	7.70	3.20
		1380	2.3	15.1	350	460	22.0	8.57	2.88
		1690	2.4	16.1	350	460	21.5	9.33	2.64
		2000	2.5	17.7	350	460	21.0	10.53	2.34
		2310	2.6	19.1	350	460	21.0	11.42	2.15

TABLE 13

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Bleed Rate B: 1.25×10^{-5} gm.moles/cm² sec

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		N × 10 ⁶ gm.moles/cm ² sec.		B/N A
			P _i	P _f		Membrane	Gas			
13	A	1069	0.0	7.5	350	300	27.5	5.09		2.46
		1380	1.9	10.4	350	300	27.0	5.76		2.17
		1690	2.0	11.7	350	300	27.5	6.56		1.90
		2000	2.1	13.1	356	300	27.5	7.45		1.68
		2310	2.2	13.9	350	300	27.0	7.94		1.57
13	A	1069	2.0	10.4	350	340	26.5	5.71		2.13
		1380	2.1	12.5	350	340	26.5	7.09		1.76
		1690	2.2	13.6	350	340	26.5	7.76		1.61
		2000	2.3	14.9	350	340	26.5	8.57		1.46
		2310	2.4	16.5	350	340	26.5	9.59		1.30
13	A	1069	2.0	12.5	350	380	26.0	7.14		1.75
		1380	2.2	14.3	350	380	26.0	8.25		1.51
		1690	2.3	15.5	350	380	25.0	9.01		1.39
		2000	2.4	18.6	392	380	25.0	9.91		1.26
		2310	2.6	21.1	420	380	25.0	10.53		1.19
13	A	1069	2.2	13.3	350	420	24.0	7.63		1.64
		1380	2.4	15.1	350	420	24.0	8.70		1.44
		1690	2.4	16.7	350	420	24.0	9.82		1.27
		2000	2.6	17.7	350	420	23.0	10.40		1.20
		2310	2.7	19.1	350	420	23.0	11.29		1.11

TABLE 13 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N A
			P_i	P_f		Membrane	Gas		
13	A	1069	2.3	13.9	350	460	23.0	7.99	1.57
		1380	2.4	15.9	350	460	22.5	9.33	1.34
		1690	2.5	17.4	350	460	22.5	10.26	1.22
		2000	2.6	18.5	350	460	22.5	10.98	1.14
		2310	2.7	19.9	350	460	22.5	11.87	1.05

TABLE 14

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Bleed Rate B: 3.24×10^{-5} gm.moles/cm² sec.

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp., °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N A
			P_i	P_f		Membrane	Gas		
14	A	1069	0.0	7.7	350	300	26.0	5.26	6.16
		1380	1.8	10.6	350	300	26.0	5.98	5.42
		1690	2.0	12.0	350	300	26.0	6.83	4.75
		2000	2.0	13.1	350	300	26.0	7.56	4.28
		2310	2.2	14.3	350	300	26.0	8.25	3.93
14	A	1069	1.9	10.9	350	340	26.0	6.11	5.30
		1380	2.0	12.9	350	340	26.0	7.41	4.38
		1690	2.1	14.3	350	340	26.0	8.30	3.90
		2000	2.4	15.7	350	340	26.0	9.06	3.58
		2310	2.5	17.1	350	340	26.0	9.91	3.27

TABLE 14 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P _i	P _f		Membrane	Gas		
14	A	1069	2.0	12.6	350	380	25.0	7.23	4.48
		1380	2.2	14.3	350	380	25.0	8.30	3.90
		1690	2.4	15.7	350	380	25.0	9.10	3.56
		2000	2.5	17.4	350	380	25.0	10.17	3.18
		2310	2.6	18.4	350	380	25.0	10.80	3.00
14	A	1069	2.2	13.4	350	420	24.5	7.67	4.23
		1380	2.3	15.3	350	420	24.5	8.90	3.64
		1690	2.4	16.7	350	420	24.5	9.82	3.30
		2000	2.6	18.3	350	420	24.5	10.75	3.02
		2310	2.7	19.5	350	420	24.5	11.51	2.81
14	A	1069	2.2	14.1	350	460	24.5	8.12	3.99
		1380	2.4	16.3	350	460	24.5	9.53	3.40
		1690	2.5	17.6	350	460	24.5	10.35	3.13
		2000	2.6	19.3	350	460	25.0	11.42	2.84
		2310	2.8	20.9	350	460	26.0	12.31	2.62

TABLE 15

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 21.5% CO₂, 78.5% H₂
Bleed Rate B: 0.86×10^{-5} gm.moles/cm² sec.

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.		B/N A
			P _i	P _f		Membrane	Gas			
15	A	1069	0.0	7.7	350	300	27.5	5.22		1.64
		1380	1.9	10.6	350	300	27.5	5.89		1.45
		1690	2.0	11.2	350	300	27.0	6.25		1.37
		2000	2.1	12.3	350	300	27.0	6.92		1.24
		2310	2.2	13.7	350	300	26.5	7.81		1.10
15	A	1069	1.9	11.2	350	340	26.0	6.34		1.50
		1380	2.0	12.5	350	340	26.0	7.14		1.20
		1690	2.1	13.4	350	340	26.0	7.70		1.11
		2000	2.4	15.4	350	340	26.0	8.88		0.96
		2310	2.5	16.6	350	340	27.0	9.55		0.90
15	A	1069	2.0	12.6	350	380	30.5	7.14		1.20
		1380	2.2	14.4	350	380	29.0	8.21		1.04
		1690	2.4	15.4	350	380	29.0	8.75		0.98
		2000	2.5	16.4	353	380	28.5	9.33		0.92
		2310	2.6	18.0	350	380	28.0	10.44		0.82
15	A	1069	2.2	13.7	350	420	27.5	7.81		1.09
		1380	2.3	15.3	350	420	27.0	8.80		0.97
		1690	2.4	16.3	350	420	27.0	9.46		0.90
		2000	2.4	17.4	350	420	27.0	10.17		0.84
		2310	2.6	18.9	350	420	27.0	11.07		0.77

TABLE 15 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P_i	P_f		Membrane	Gas		
15	A	1069	2.2	14.3	350	460	27.0	8.23	1.04
		1380	2.4	16.1	350	460	27.0	9.28	0.92
		1690	2.5	17.0	350	460	27.0	9.82	0.87
		2000	2.6	18.0	350	460	27.0	10.44	0.82
		2310	2.8	19.9	350	460	27.0	11.60	0.75

TABLE 16

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

Bleed Rate B: 2.32×10^{-5} gm.moles/cm² sec.

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N _A
			P_i	P_f		Membrane	Gas		
16	A	1069	0.0	7.9	350	300	28.0	5.35	4.34
		1380	1.8	10.8	350	300	28.0	6.11	3.80
		1690	2.0	14.7	448	300	28.0	6.69	3.47
		2000	2.0	12.3	350	300	28.0	6.96	3.33
		2310	2.2	13.9	350	300	28.0	7.94	2.92
16	A	1069	2.2	13.4	350	420	27.5	7.58	3.06
		1380	2.3	15.3	350	420	27.5	8.81	2.63
		1690	2.6	17.6	350	420	26.5	10.22	2.26
		2310	2.8	19.1	350	420	26.5	11.10	2.10

TABLE 16 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.	B/N A
			P_1	P_f		Membrane	Gas		
16	A	1069	2.2	14.1	350	460	27.0	8.08	2.87
		1380	2.4	16.2	350	460	26.5	9.37	2.48
		1690	2.5	17.6	350	460	26.5	10.26	2.26
		2000	2.6	18.4	350	460	26.5	10.75	2.16
		2310	2.8	20.1	350	460	28.0	11.69	1.99

TABLE 18

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANEFeed Gas Composition: 21% CO, 79% H₂

Expt. No.	Procedure	Bleed Rate B: 2.52×10^{-5} gm.moles/cm sec.										$N_A \times 10^6$ gm.moles/cm sec.
		Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp: °C		Gas	Membrane			
			P _i	P _f								
18	A	1069	0.4	0.9	1623	300		27.5			0.07	
		1380	0.4	0.9	1200			27.5			0.10	
		1690	0.3	0.8	1200			27.5			0.10	
		2000	0.3	0.9	1200			27.0			0.12	
		2310	0.3	0.9	1200			27.0			0.12	
18	A	1069	0.3	0.9	1200	340		27.0			0.12	
		1690	0.4	0.9	1200			27.0			0.10	
		2310	0.4	1.3	1200			27.0			0.18	
18	A	1069	0.8	2.3	350	380		25.5			1.03	
		1380	0.9	2.9	350			25.5			1.36	
		1690	1.0	3.7	350			25.0			1.88	
		2000	1.2	4.3	350			25.0			2.12	
		2310	1.4	5.9	350			25.0			3.08	
18	A	1069	1.8	10.2	350	420		24.5			5.76	
		1380	1.9	9.9	350			24.5			5.49	
		1690	1.8	10.2	350			24.5			5.76	
		2000	2.0	12.45	350			24.5			7.18	
		2310	2.2	14.3	350			23.5			8.30	

TABLE 18 (Continued)

<u>Expt. No.</u>	<u>Procedure</u>	<u>Pressure</u> <u>mm Hg</u>	<u>Pressure, mm Hg</u>		<u>Time</u> <u>Secs</u>	<u>Temp. °C</u>		$N_A \times 10^6$ <u>gm.moles/cm² sec.</u>
			<u>P_i</u>	<u>P_f</u>		<u>Membrane</u>	<u>Gas</u>	
18	A	1069	2.0	12.2	350	460	23.5	7.00
		1380	2.2	13.5	350		23.5	7.76
		1690	2.2	14.5	350		23.0	8.46
		2000	2.4	16.0	350		23.0	9.37
		2310	2.5	17.6	350		23.0	10.40

TABLE 19

EFFECT OF IMPURITIES ON THE RATE OF TRANSPORT OF HYDROGEN
THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: Pure hydrogen, stop cock grease
present near the membrane

Bleed Rate B: NONE

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm. moles/cm ² sec.
			P_i	P_f		Membrane	Gas	
19	A	1069	0.0	3.4	1200	300	26.0	0.67
		1380	0.7	5.0	1200	300	26.0	0.83
		1690	0.8	7.7	1200	300	26.0	1.37
		2000	1.0	11.2	1200	300	26.0	2.03
		2310	1.2	14.5	1200	300	26.0	2.64
19	A	1069	1.0	11.2	1200	340	25.0	2.03
		1380	1.3	14.5	1200	340	25.0	2.63
		1690	1.4	18.9	1200	340	25.0	3.48
		2000	1.5	24.2	1200	340	25.0	4.51
		2310	1.8	10.8	350	340	25.0	6.69
19	A	1069	1.4	6.5	350	380	24.5	3.50
		1380	1.5	8.1	350	380	24.5	4.51
		1690	1.7	10.2	350	380	24.8	5.80
		2000	2.0	12.4	350	380	24.8	7.09
		2310	2.3	15.6	354	380	24.8	9.01
19	A	1069	1.6	8.4	350	420	24.8	4.64
		1380	1.8	10.4	350	420	24.8	5.89
		1690	2.0	12.9	350	420	24.5	7.45
		2000	2.3	15.5	350	420	24.5	9.04
		2310	2.6	18.9	350	420	24.5	11.15

TABLE 19 (Continued)

Expt. No.	Procedure	Pressure mm Hg	Pressure, mm Hg		Time Secs	Temp. °C		$N_A \times 10^6$ gm.moles/cm ² sec.
			P_i	P_f		Membrane	Gas	
19	A	1069	1.8	9.9	350	460	24.5	5.53
		1380	2.0	12.6	350	460	24.5	7.25
		1690	2.2	15.3	350	460	24.8	8.97
		2000	2.4	18.0	350	460	24.8	10.66
		2310	2.7	20.7	350	460	24.8	12.32

$$\Delta P = P_f - P_i, \text{ mm Hg}$$

Substituting the corresponding numerical values, Equation (101) becomes:

$$N_A = \frac{5641}{(1.268)(6.236 \times 10^4)} \frac{\Delta P}{\phi T} = 7.14 \times 10^{-2} \frac{\Delta P}{\phi T} \quad (102)$$

Equation (102) is the working equation for calculating the transport rate per unit area from the experimental data. The values of N_A are also tabulated in Tables 1-19.

B. Determination of the Diffusivity of Hydrogen in Palladium-Silver Alloy

The diffusivity of hydrogen in palladium-silver alloy may be determined from Equation (30) and the diffusion flux from Table 1 and Table 2.

The assumptions for these calculations are (1) Equation (30) is accurate enough for the purpose of these calculations, (2) the adsorption and dissociation process is fast compared to diffusion in the solid so that equilibrium exists between the gas phase and the palladium-silver surface.

Using Equation (80) therefore

$$N_A = \frac{DC}{L} \quad (103)$$

but

$$C = r\theta \frac{\text{at.H}}{\text{at.Pd-Ag}} \times \frac{\text{gm.moles H}_2}{2 \text{ at.H}} \times \frac{\text{gm. at.Pd-Ag}}{107 \text{ gm.Pd-Ag}} \\ \times \frac{11.62 \text{ gm.Pd-Ag}}{\text{cm}^3 \text{ Pd-Ag}}$$

also

$$L = 0.0102 \text{ cm}$$

$$r = 0.36$$

therefore

$$D = \frac{(0.0102)(2)(107)}{(11.62)(0.36)} \times \frac{N_A}{\theta} \quad (104)$$

Equation (104) is the working equation for determining the diffusivity.

From the tabulated values of N_A in Table 1 and Table 2, and calculated values of θ from Equation (30), the values of D for different temperatures are calculated and tabulated in Table 20 and Table 21. An average value of D is taken for each temperature in the pressure range. The logarithm of these values are plotted against $1000/T$ in Figure 12. Figure 12 indicates a relationship of the form:

$$D = D_0 \exp\left(-\frac{\Delta E_D}{RT}\right) \quad (105)$$

where D_0 = constant

ΔE_D = energy of activation of diffusion

From Figure 12 the value of D at a particular temperature is found to be given by:

$$D = 5.9 \times 10^{-3} \exp\left(-\frac{6,560}{RT}\right) \quad (106)$$

This is compared with an accepted value (23) of

$$D = 4.3 \times 10^{-3} \exp\left(-\frac{5,600}{RT}\right) \quad (107)$$

for pure palladium at high temperature; although D_0 is roughly the same in both cases, the activation for diffusion differs in the two materials.

C. Temperature and Pressure Dependency of Flux of Pure Hydrogen in Palladium-Silver Alloy

The fluxes recorded in Tables 1 and 2 are plotted as $\log N_A$ versus $\log P_{\text{mm}}$. A straight line relationship is found as shown in

TABLE 20
DIFFUSIVITY OF HYDROGEN IN PALLADIUM-SILVER: PROCEDURE A

Temp. °C	Pressure mm Hg	$N_A \times 10^6$ gm.moles/cm ² sec.	θ	$\frac{N}{\theta} \times 10^5$	$D \times 10^5$ cm ² /sec.
300	1069	7.41	0.210	3.53	1.84
300	1380	8.75	0.250	3.50	1.83
300	1690	9.95	0.290	3.43	1.79
300	2000	10.84	0.330	3.28	1.71
300	2310	12.09	0.365	3.31	1.73
					$D_{ave} = 1.78$
340	1069	8.17	0.155	5.27	2.75
340	1380	9.62	0.180	5.34	2.79
340	1690	10.89	0.205	5.31	2.77
340	2000	11.82	0.230	5.14	2.68
340	2310	13.21	0.248	5.33	2.78
					$D_{ave} = 2.75$
380	1069	8.88	0.125	7.10	3.70
380	1380	9.64	0.145	6.65	3.47
380	1690	11.51	0.160	7.19	3.75
380	2000	12.58	0.175	7.19	3.75
380	2310	13.83	0.190	7.28	3.80
					$D_{ave} = 3.69$
420	1069	9.17	0.100	9.17	4.78
420	1380	10.71	0.115	9.31	4.86
420	1690	12.14	0.125	9.71	5.07
420	2000	13.25	0.140	9.46	4.94
420	2310	14.46	0.150	9.64	5.03
					$D_{ave} = 4.94$

TABLE 20 (Continued)

Temp. °C	Pressure mm Hg	$N_A \times 10^6$ mg.moles/cm ² sec.	θ	$\frac{N}{\theta} \times 10^5$	$D \times 10^5$ cm ² /sec.
460	1069	9.91	0.080	12.39	6.46
460	1380	11.51	0.095	12.12	6.32
460	1690	12.98	0.105	12.36	6.45
460	2000	14.01	0.120	11.67	6.09
460	2310	15.62	0.125	12.50	6.52
					$D_{ave} = 6.37$

TABLE 21

DIFFUSIVITY OF HYDROGEN PALLADIUM-SILVER: PROCEDURE B

Temp. °C	Pressure mm Hg	$N_A \times 10^6$ mg.moles/cm ² sec.	θ	$\frac{N}{\theta} \times 10^5$	$D \times 10^5$ cm ² /sec.
300	1069	7.05	0.210	3.36	1.75
300	1380	8.30	0.250	3.32	1.73
300	1690	9.68	0.290	3.34	1.74
300	2000	10.62	0.330	3.22	1.68
300	2310	12.45	0.365	3.41	1.78
					$D_{ave} = 1.74$
340	1069	7.94	0.155	5.12	2.67
340	1380	9.28	0.180	5.15	2.69
340	1690	10.50	0.205	5.12	2.67
340	2000	11.69	0.230	5.08	2.65
340	2310	13.21	0.248	5.33	2.78
					$D_{ave} = 2.69$

TABLE 21 (Continued)

Temp. °C	Pressure mm Hg	$N_A \times 10^6$ mg. moles/cm sec.	θ	$\frac{N}{\theta} \times 10^5$	$D \times 10^5 \text{ cm}^2/\text{sec.}$
380	1069	8.66	0.125	6.93	3.62
380	1380	10.22	0.145	7.05	3.68
380	1690	11.29	0.160	7.06	3.68
380	2000	12.58	0.170	7.19	3.75
380	2310	14.14	0.190	7.44	3.88
					$D_{\text{ave}} = 3.72$
420	1069	9.15	0.100	9.15	4.77
420	1380	10.71	0.115	9.31	4.86
420	1690	11.91	0.125	9.53	4.97
420	2000	13.30	0.140	9.50	4.96
420	2310	14.90	0.150	9.93	5.18
					$D_{\text{ave}} = 4.95$
460	1069	9.73	0.080	12.16	6.34
460	1380	11.38	0.095	11.98	6.25
460	1690	12.58	0.105	11.98	6.25
460	2000	14.06	0.120	11.72	6.11
460	2310	15.71	0.125	12.57	6.56
					$D_{\text{ave}} = 6.30$

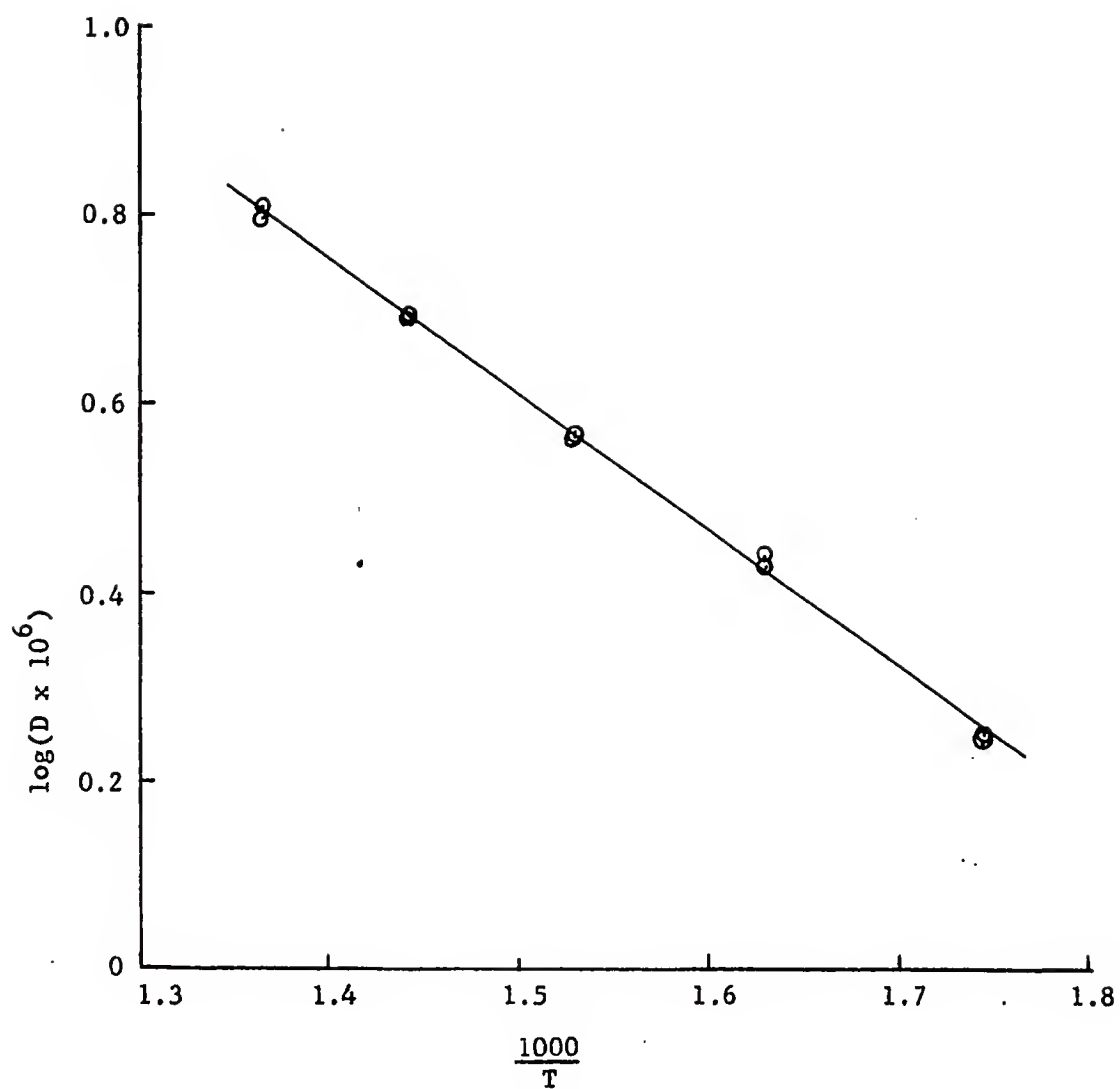


Figure 12. Diffusivity of Hydrogen
in Palladium Silver

Figure 13 and Figure 15; a plot of $\log N_A$ versus $1000/T$ also gives a straight line relationship as shown in Figure 14 and Figure 16. These results suggest that the flux is related to the pressure and temperature by:

$$N_A = k_1 P^{\frac{1}{n}} \exp\left(-\frac{\Delta E}{RT}\right) \quad (108)$$

where $k_1 = \text{constant}$

$\Delta E = \text{energy of activation}$

$\frac{1}{n} = \text{constant}$

The theoretical verification of Equation (108) can be traced back to Equation (80) in which

$$N_A = \frac{DC}{L} \quad (109)$$

but

$$D = D_0 \exp\left(-\frac{\Delta E_D}{RT}\right) \quad (110)$$

$$C = k_3 P^{\frac{1}{n}} \exp\left(-\frac{\Delta H_C}{RT}\right) \quad (111)$$

where $k_3 = \text{constant}$

$\Delta H_C = \text{heat of solution}$

The equation for C should come from Equation (30), but this can be approximated by Equation (111). Figures 17-18 show that Equation (111) is a good approximation for the ranges of the temperature and pressure used in the experiment. Equation (109) therefore becomes:

$$N_A = \frac{k_3 D_0}{L} P^{\frac{1}{n}} \exp\left(-\frac{\Delta E_D - \Delta H_C}{RT}\right) = k_1 P^{\frac{1}{n}} \exp(-\Delta E/RT) \quad (112)$$

A multiple regression analysis technique was used to correlate

B: 3.79×10^{-5} gm. moles/cm² sec.

Feed Gas Composition: Pure H₂

Procedure: A

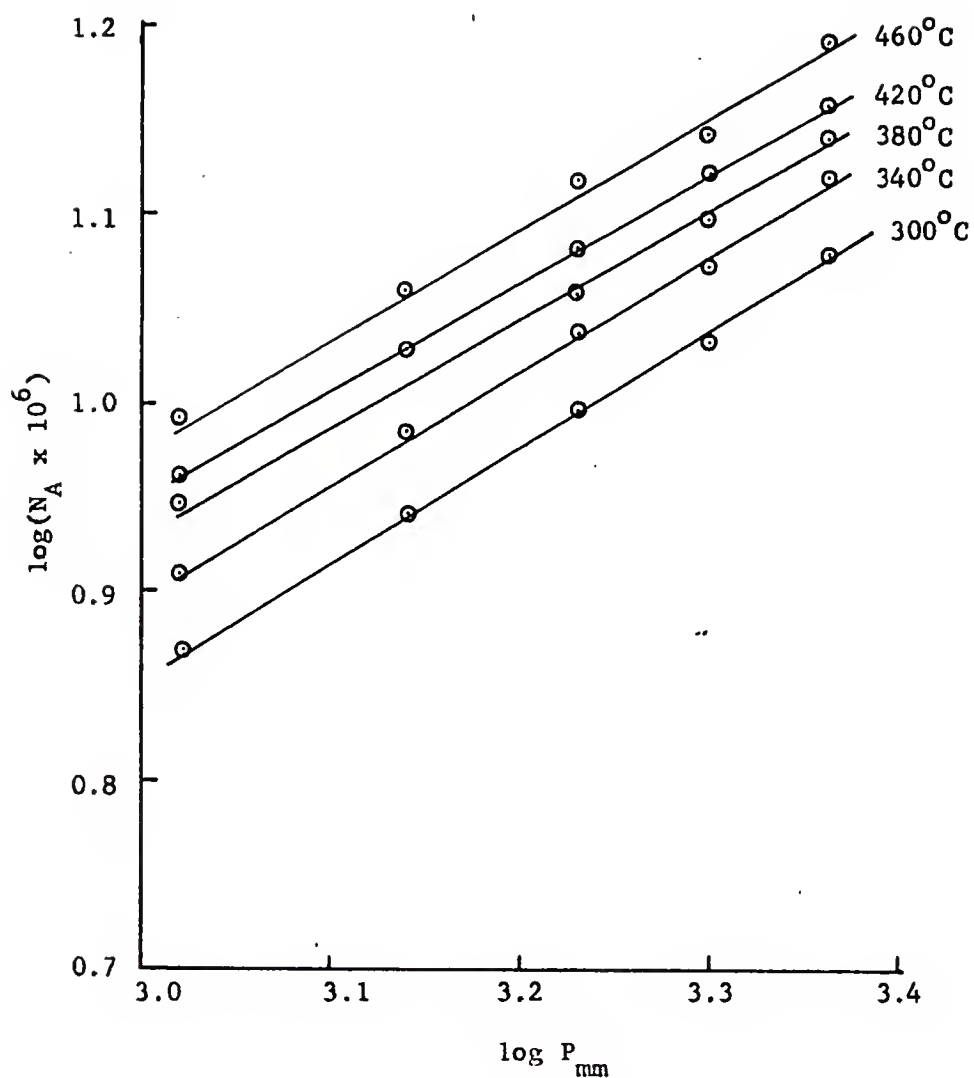


Figure 13. The Rate of Transport of Hydrogen Through Palladium-Silver Membrane at Different Temperatures

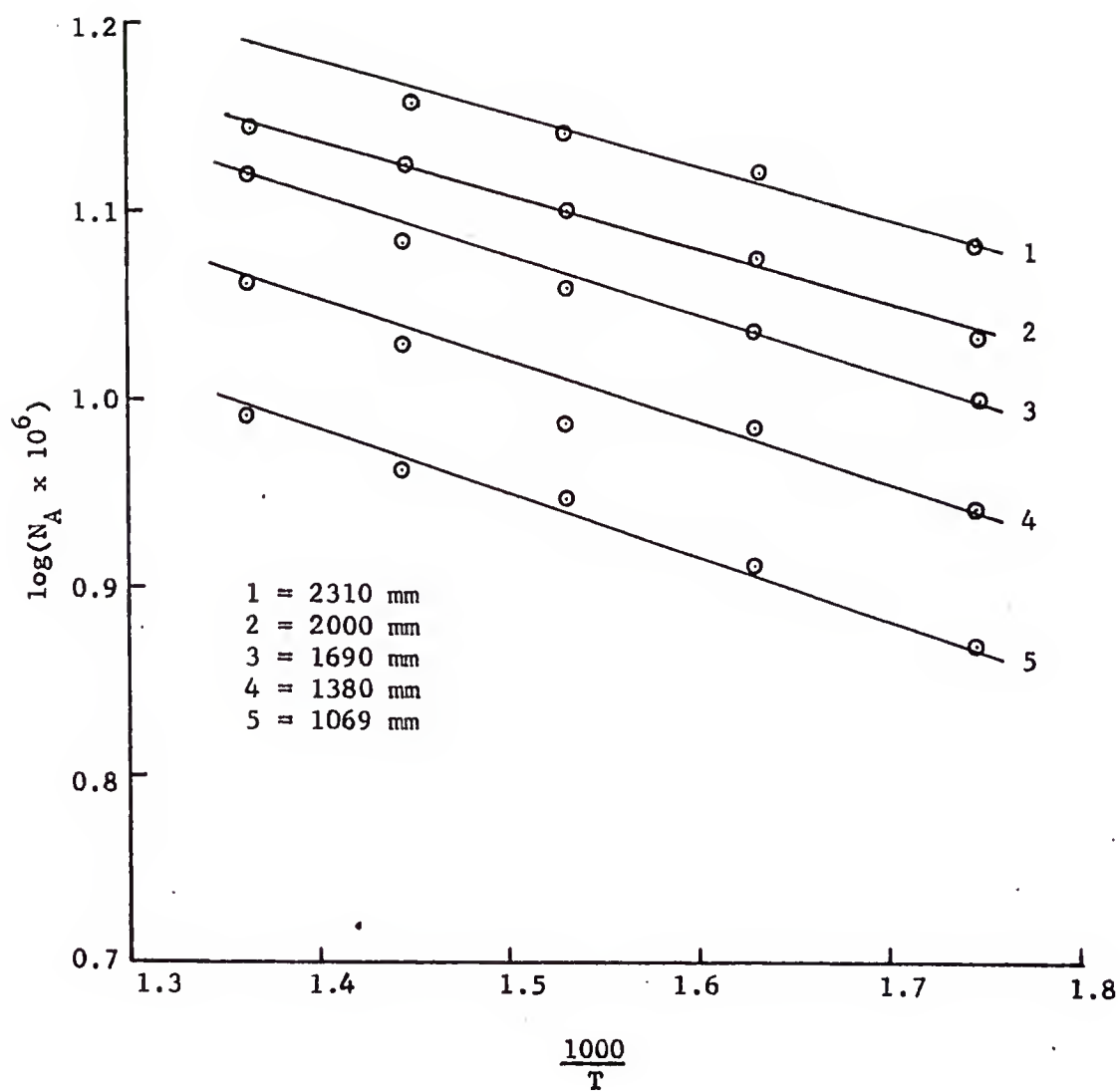


Figure 14. Determination of the Energy of Activation

B: 3.79×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: Pure H₂

Procedure: B

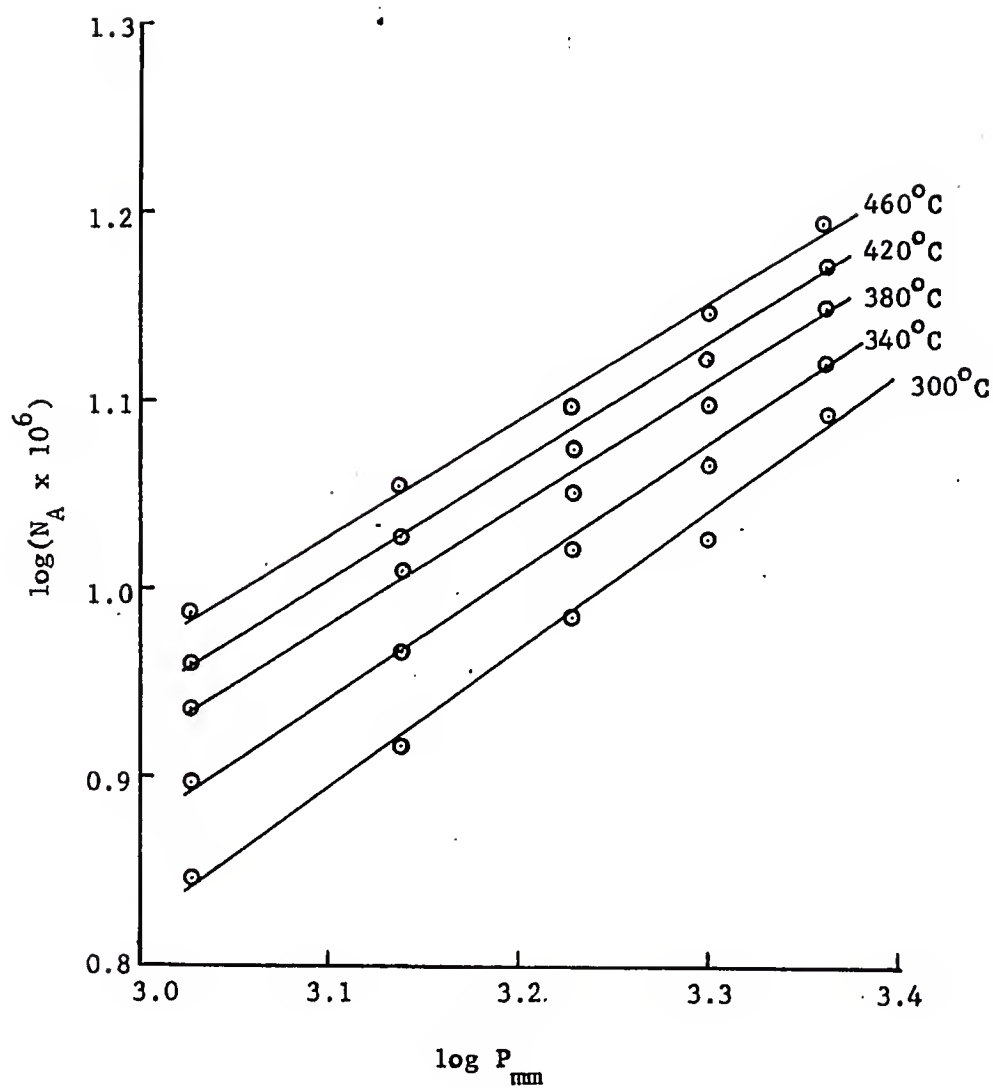


Figure 15. The Rate of Transport of Hydrogen Through Palladium Silver Membrane at Different Temperatures

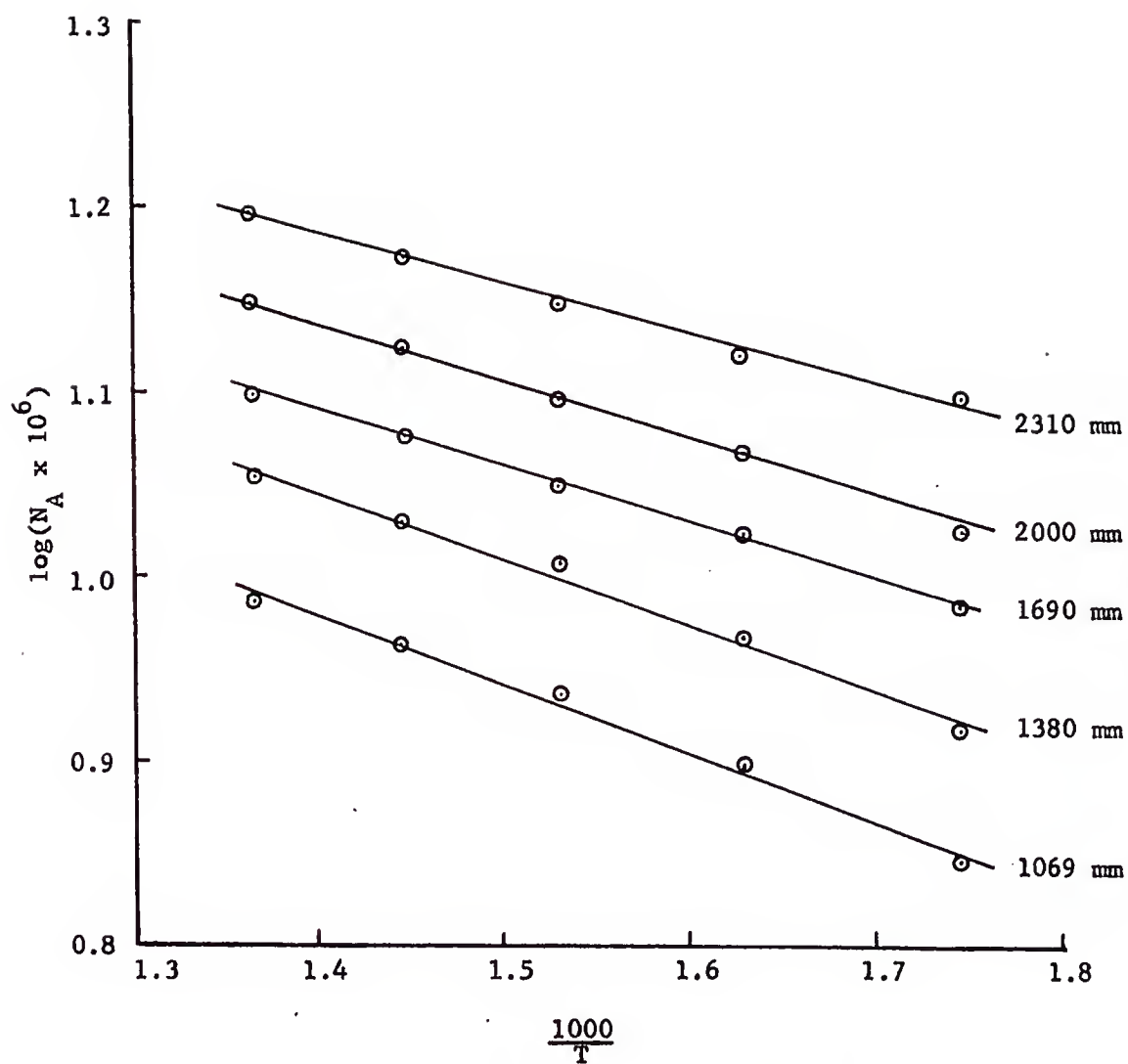


Figure 16. Determination of the Energy of Activation

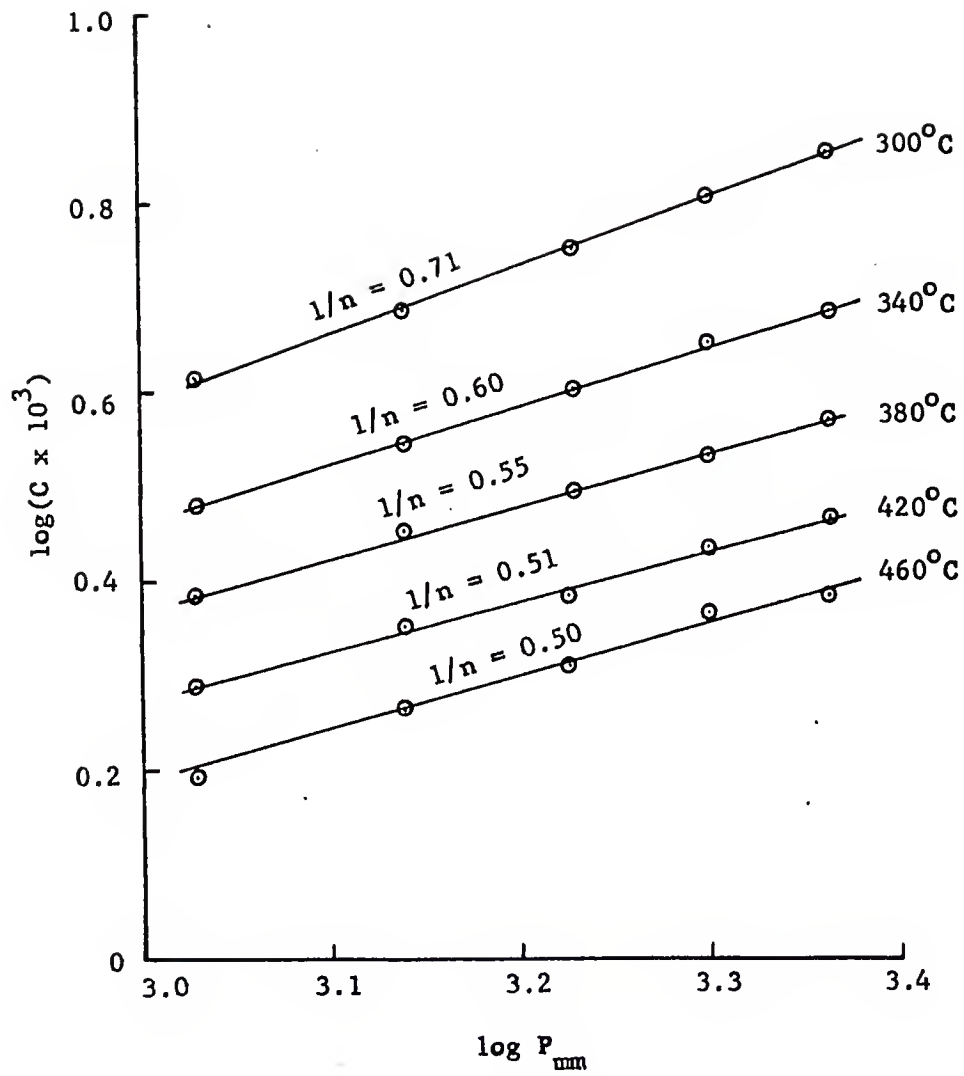


Figure 17. A Plot of Log C Versus Log P_{mm}

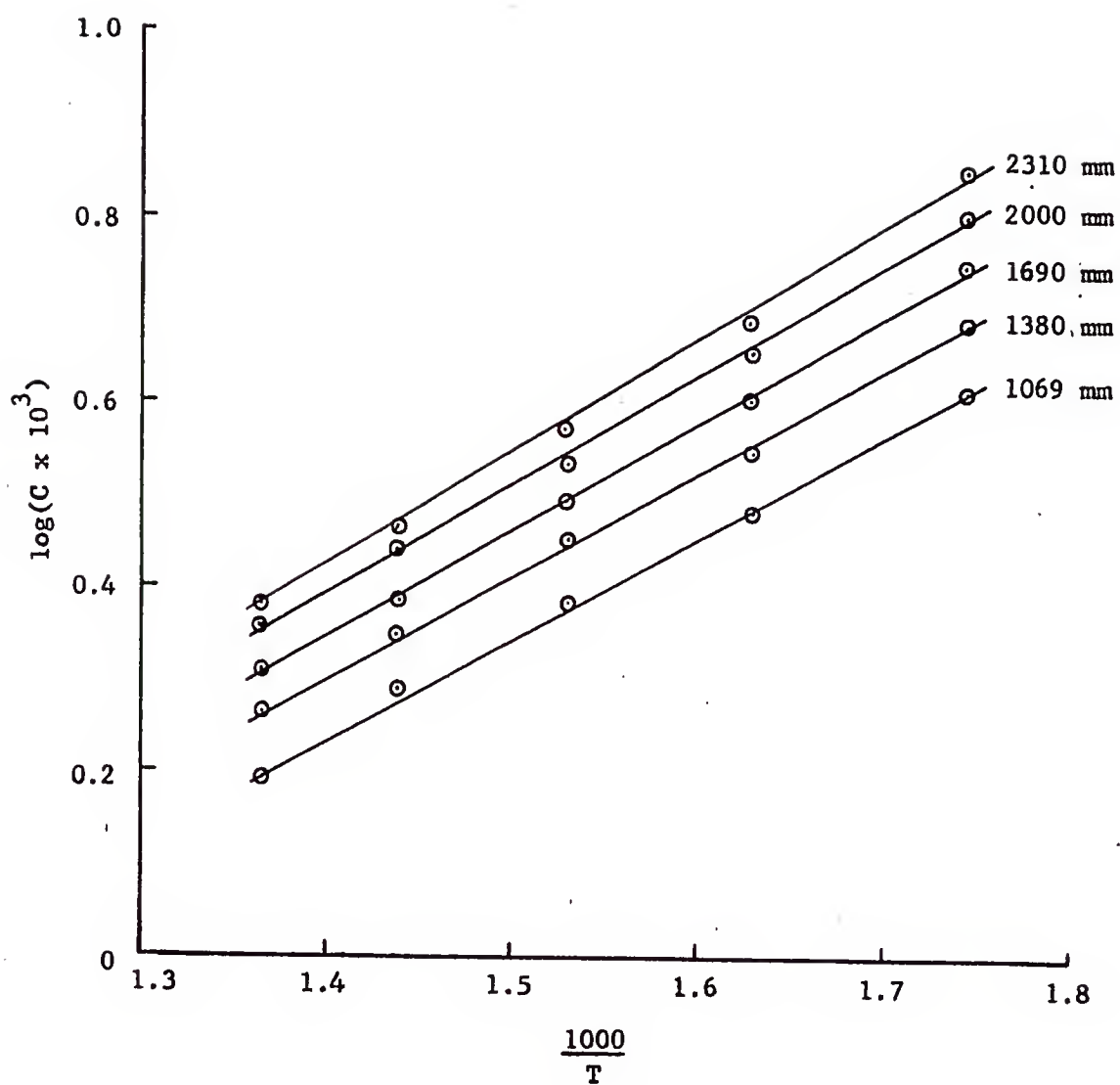


Figure 18. A Plot of Log C Versus $\frac{1000}{T}$

Equation (108) with the data. For the data in Table 1 and Table 2 this resulted in

$$N_A = 3.78 \times 10^{-7} P^{0.60} \exp \left(\frac{-1,340}{RT} \right) \quad (113)$$

$$N_A = 2.97 \times 10^{-7} P^{0.64} \exp \left(\frac{-1,460}{RT} \right) \quad (114)$$

when the feed gas is pure hydrogen.

D. Effect of Impurities on the Transport of Hydrogen Through Palladium Silver

Table 3 to Table 19 give the transport rate of hydrogen through palladium-silver membranes for different feed gas compositions and various bleed rates. Using the same kind of plot as in Figure 12 and Figure 13 of the previous section and applying similar principles to the data of Tables 3 to 19, resulted in the data shown in Figures 19 to 52. Except for carbon monoxide and for very low bleed rate, the experimental data for hydrogen diffusion in all impurities fitted Equation (108). The results of the least square fit are tabulated in Table 22. The k_1 in these tables indicate that total pressure was used in the calculation, and k_1' when partial pressure of hydrogen was used.

From the values indicated in Tables 3 to 16, it can be concluded that bleeding increases the transport rate. Equation (108) is not suitable for expressing the relationship between transport rate and bleed rate. It was found that a plot of bleed rate B , gm.moles/cm²sec., versus B/N_A gave a straight line as shown in Figures 53 to 77. The relationship is given by the equation:

B: 0.55×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

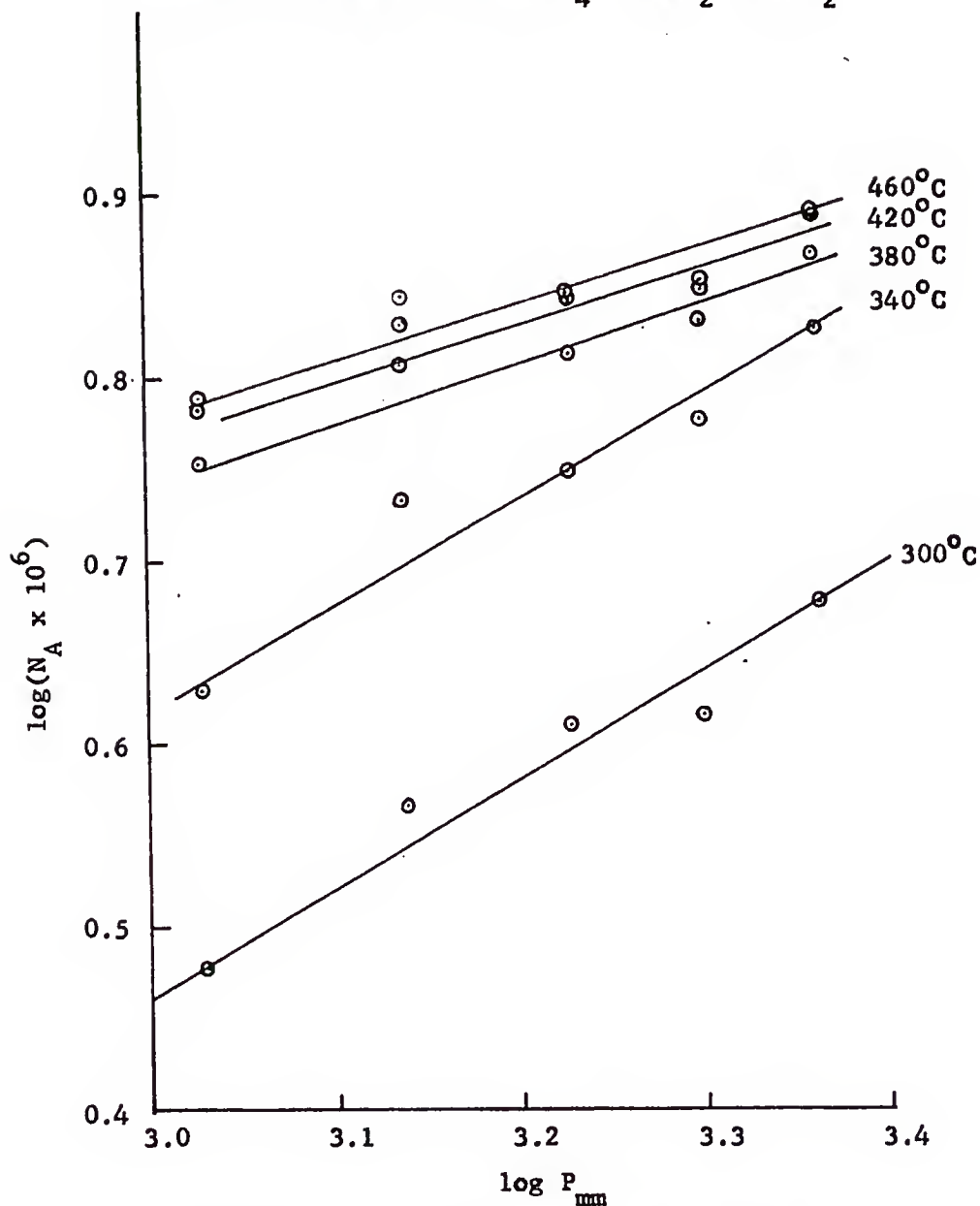


Figure 19. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

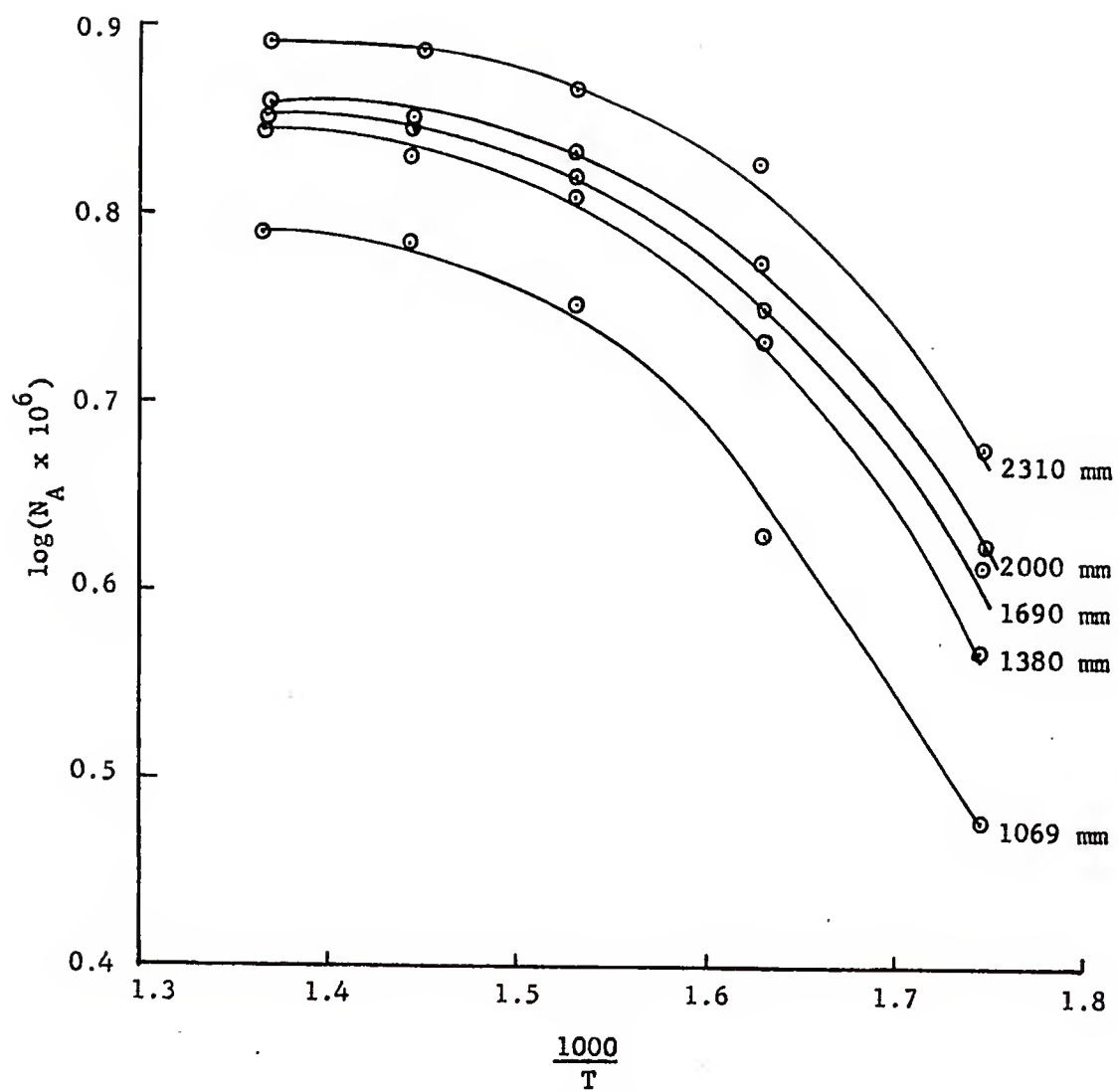


Figure 20. Determination of the Energy of Activation

B: 1.08×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

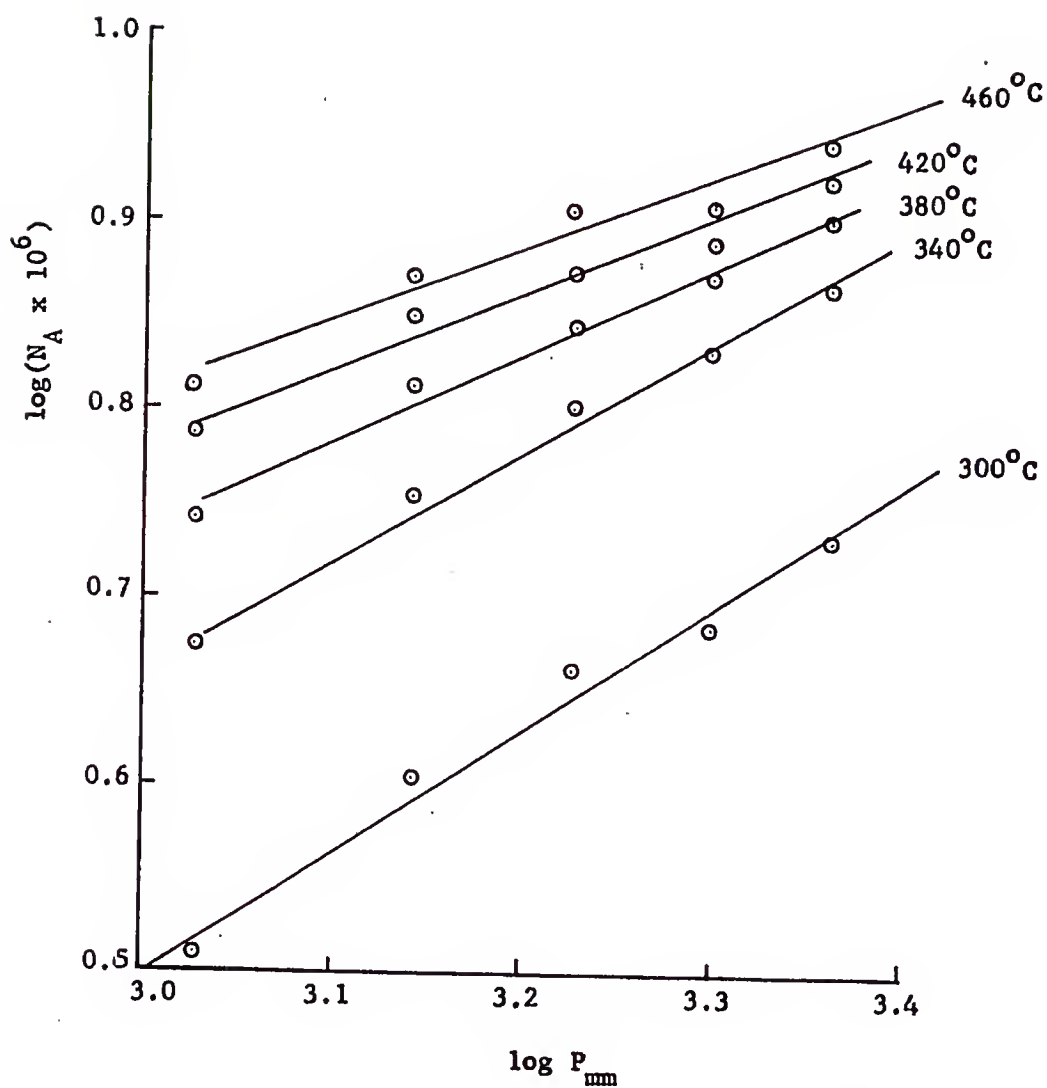


Figure 21. Effect of Impurities on the Rate of Transport of Hydrogen Through Palladium Silver Membrane

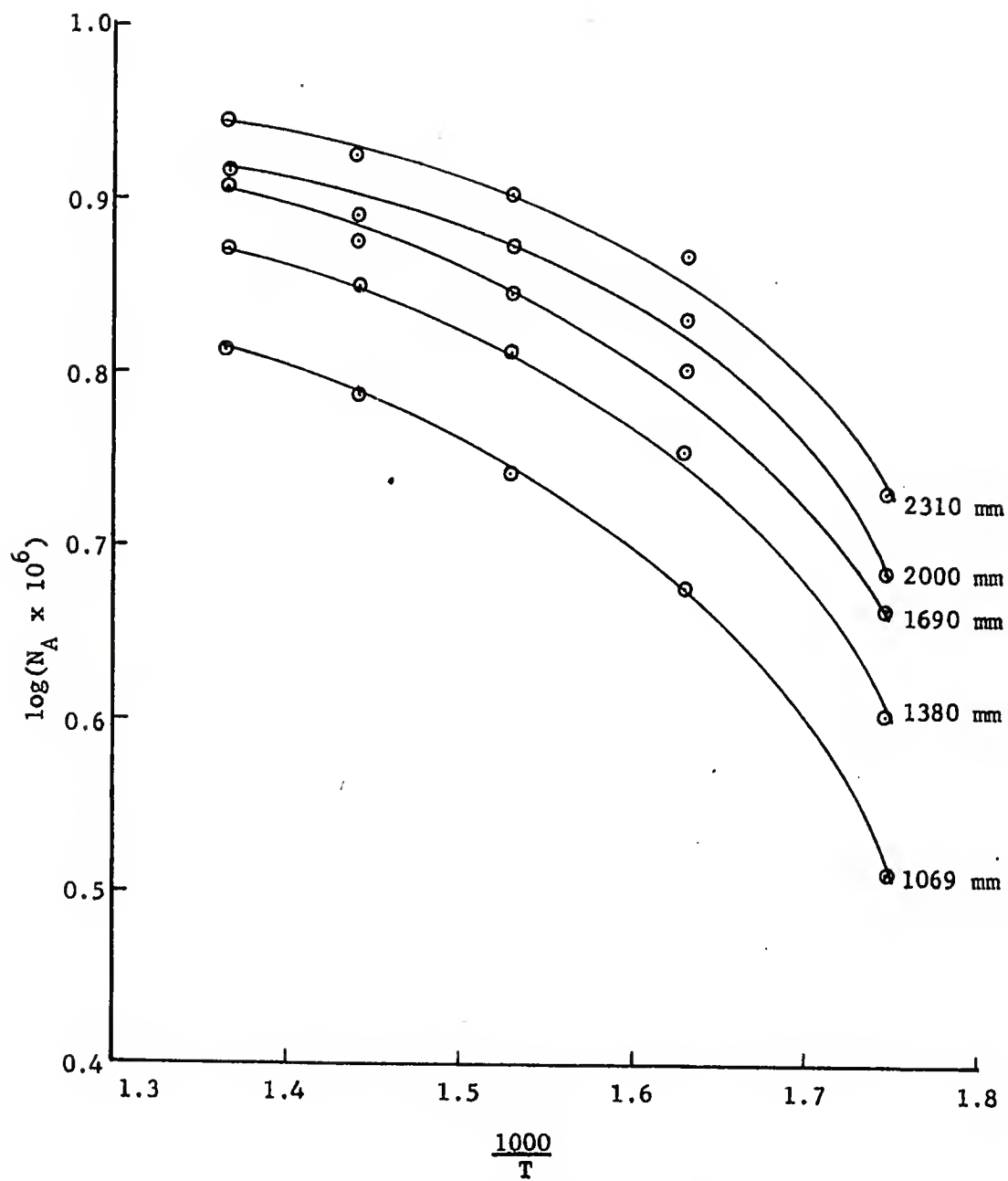


Figure 22. Determination of the Energy of Activation

B: 1.88×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

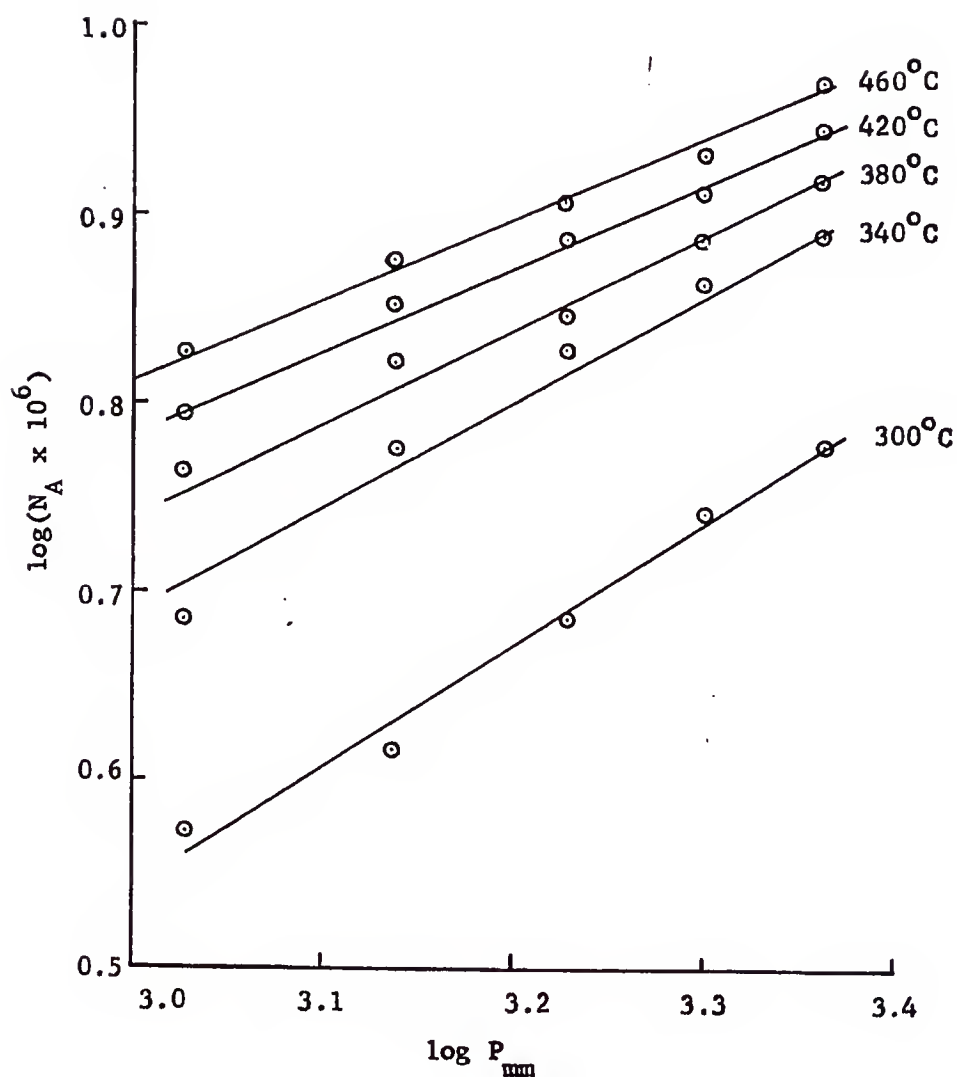


Figure 23. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

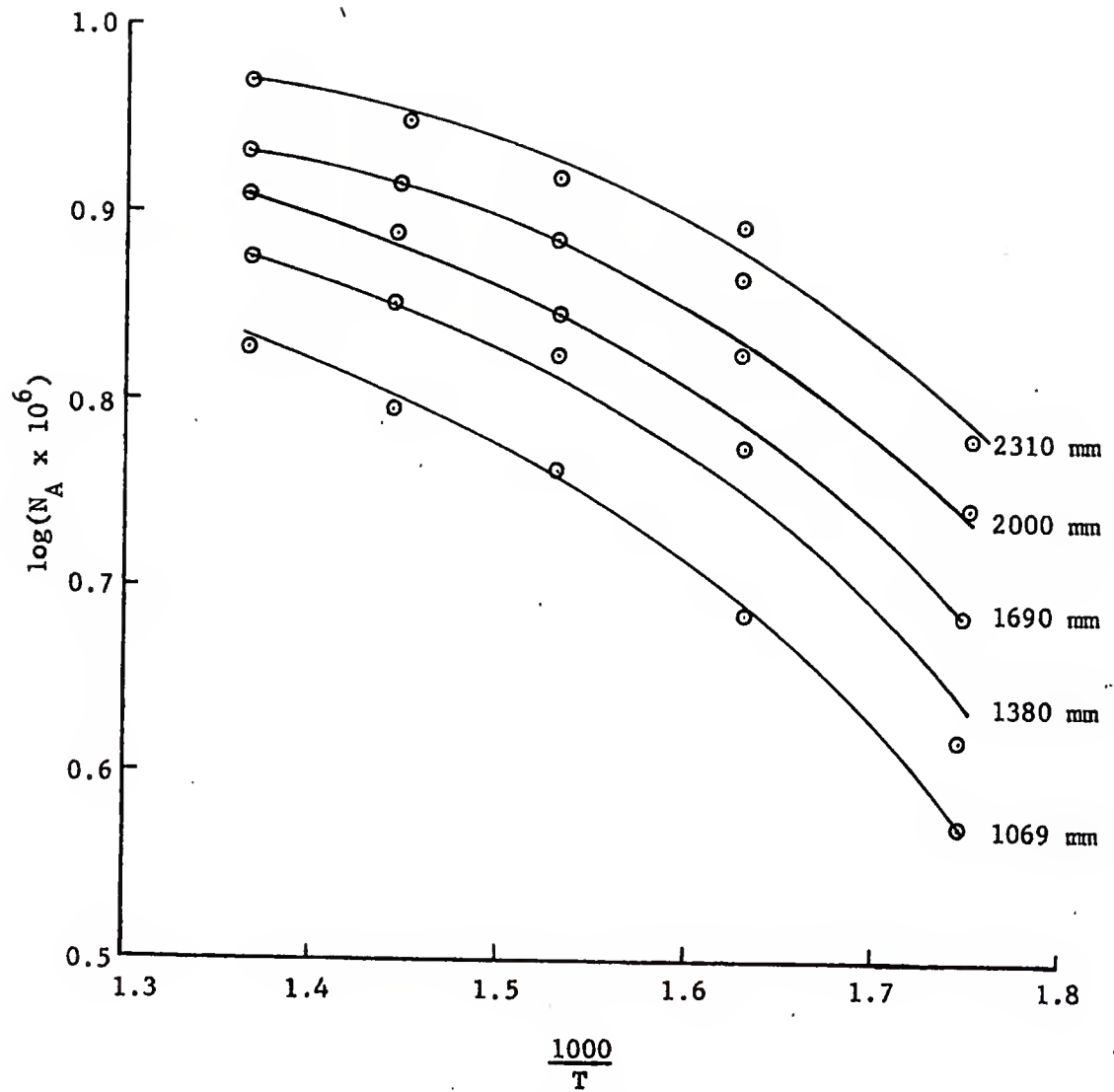


Figure 24. Determination of the Energy of Activation

B: 2.80×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

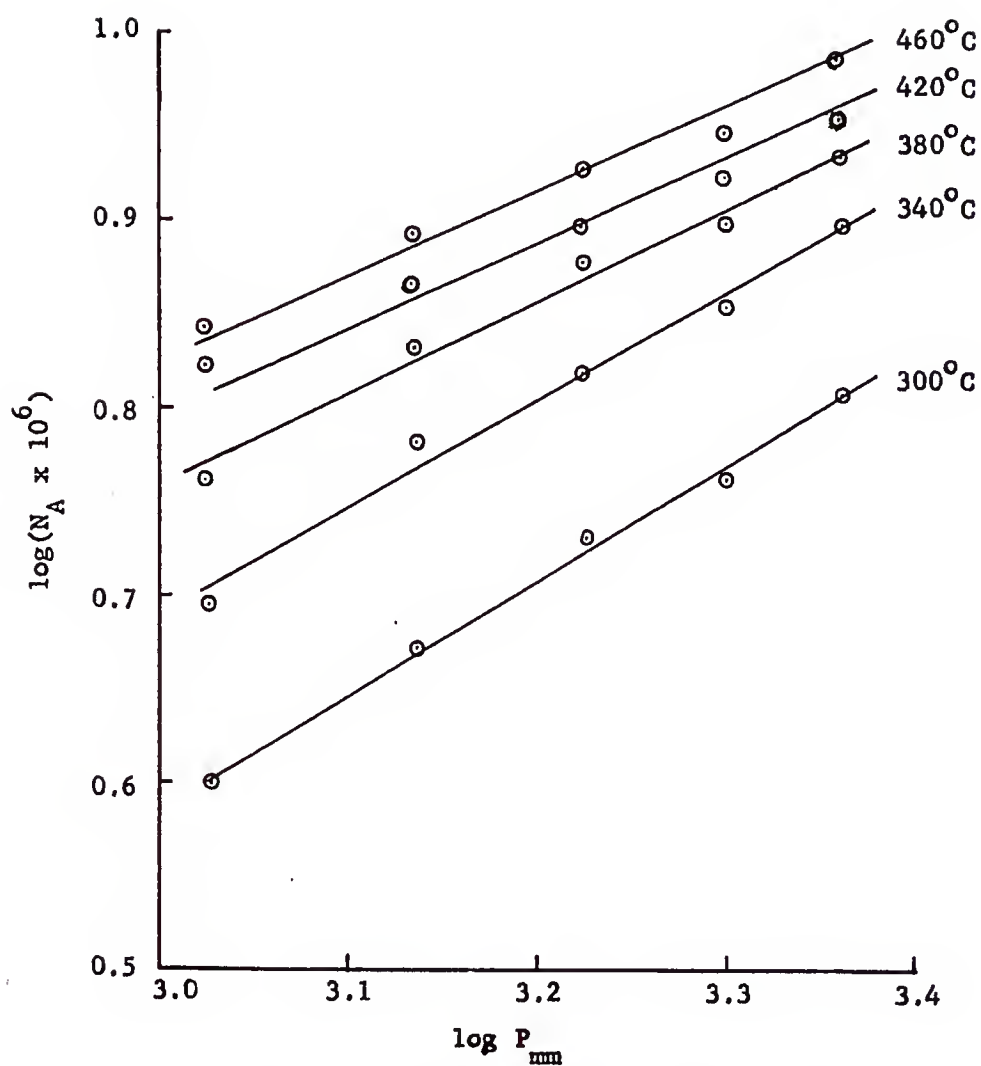


Figure 25. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

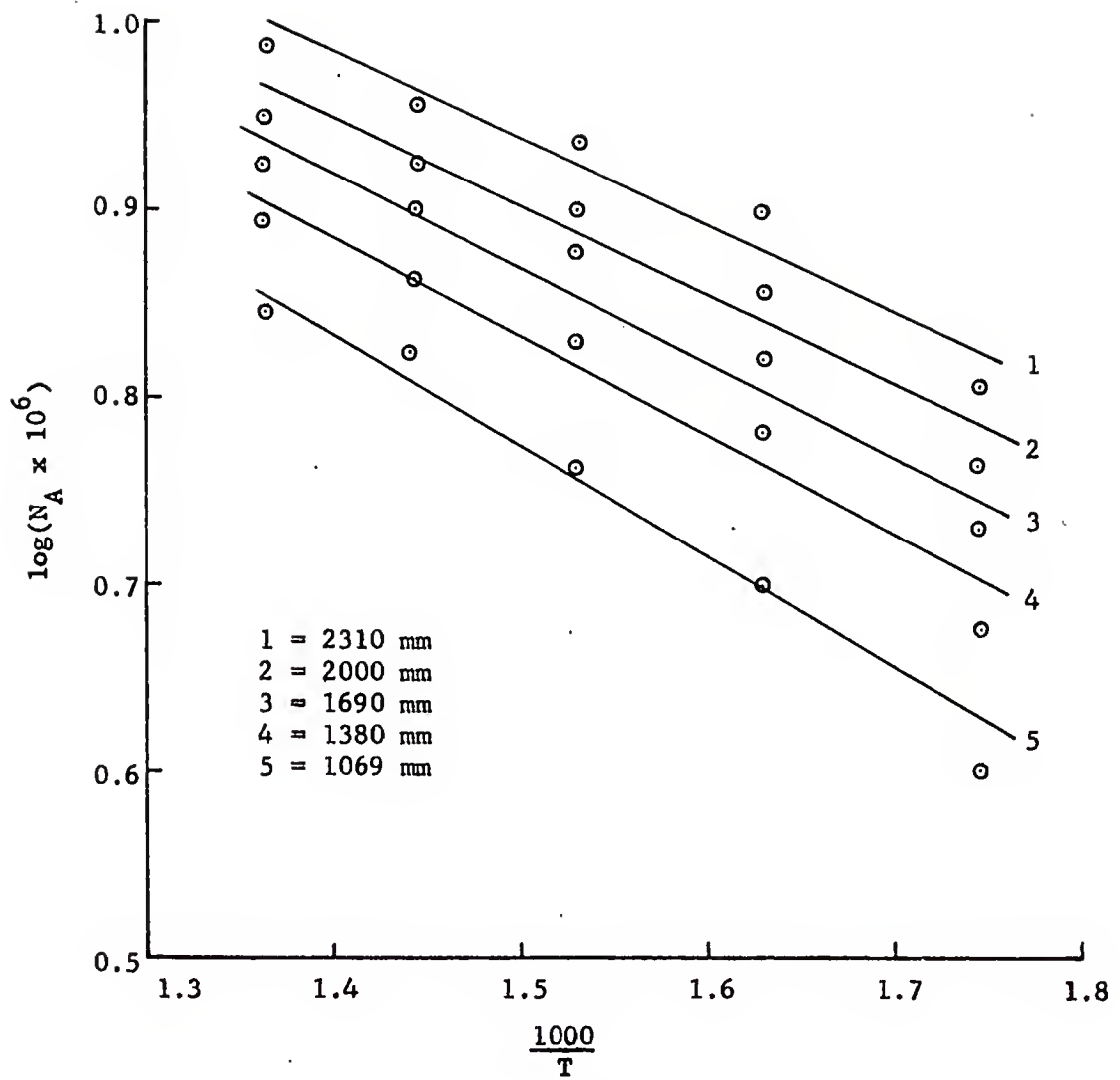


Figure 26. Determination of the Energy of Activation

B: 0.38×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

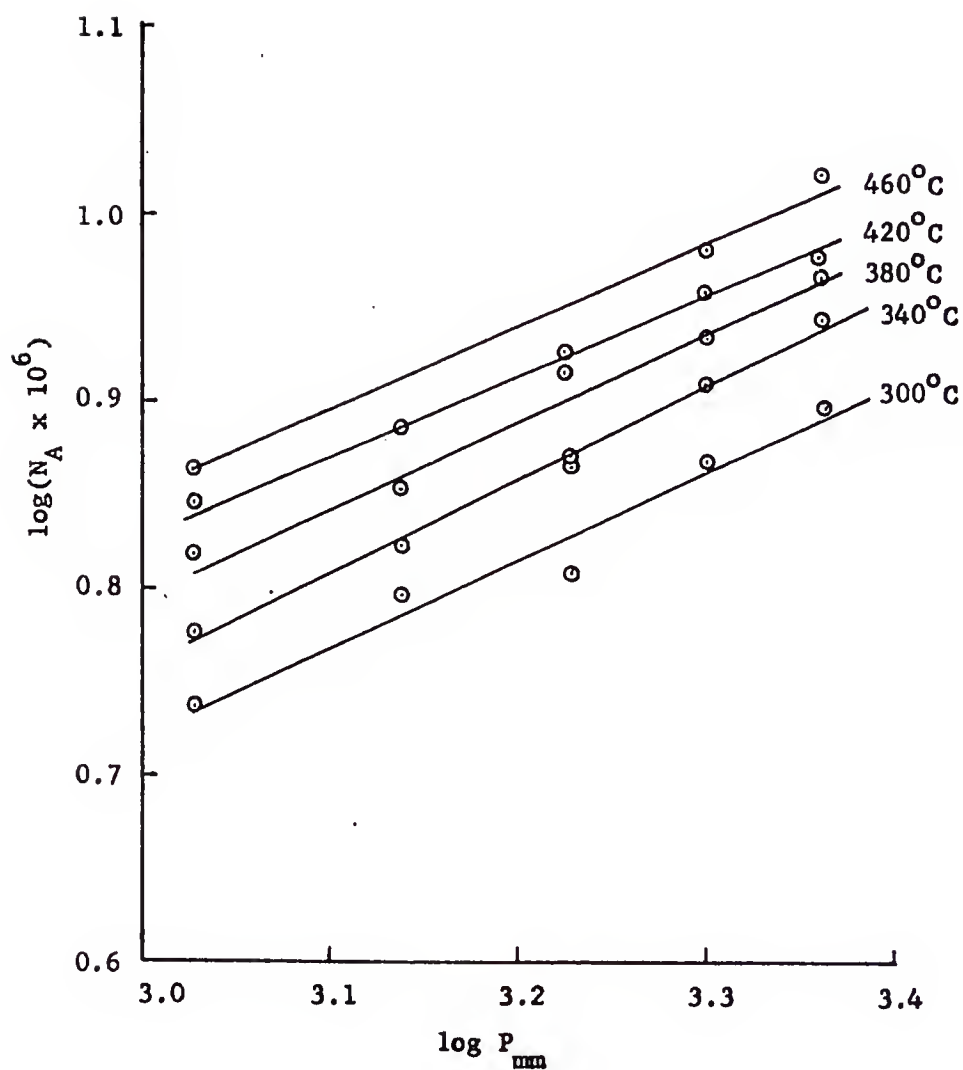


Figure 27. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

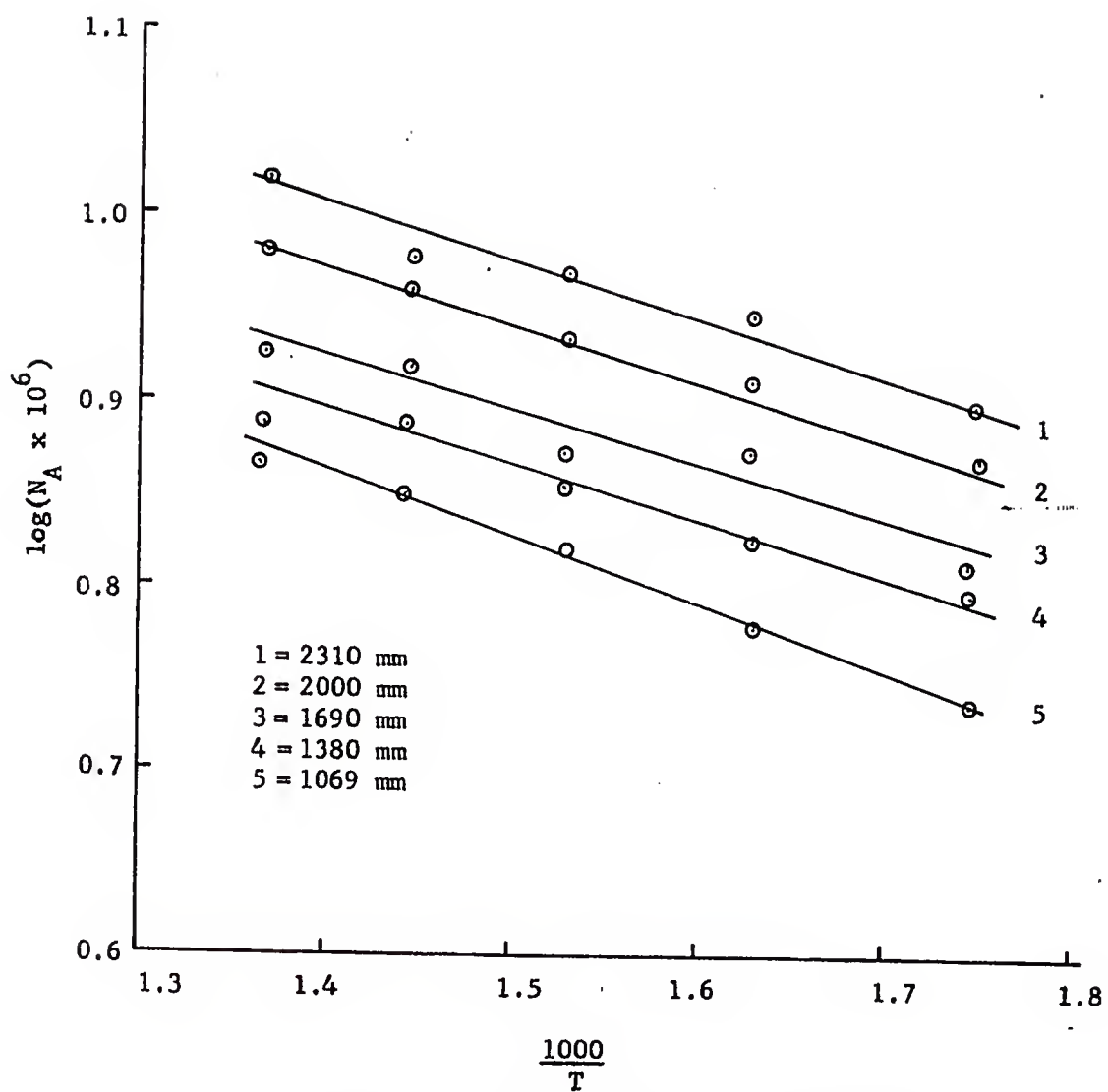


Figure 28. Determination of the Energy of Activation

B: 0.52×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

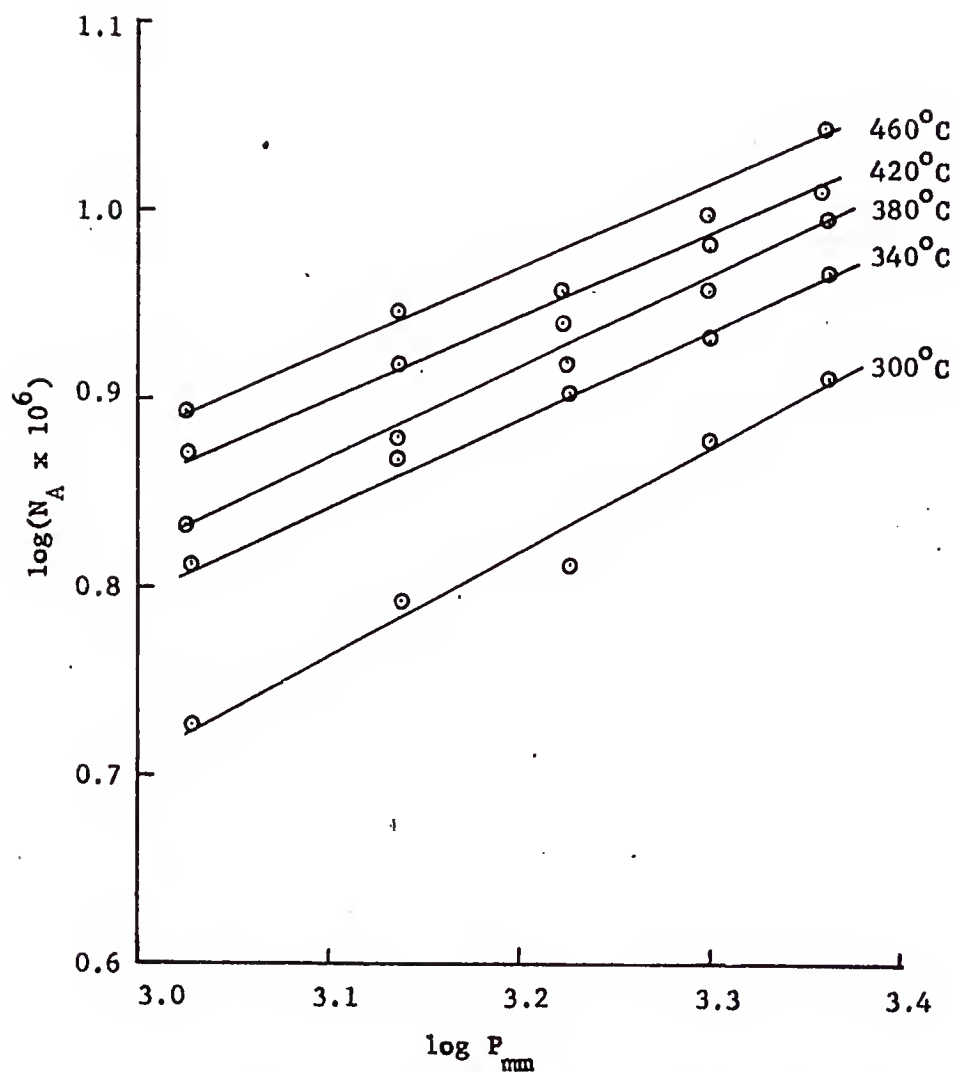


Figure 29. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

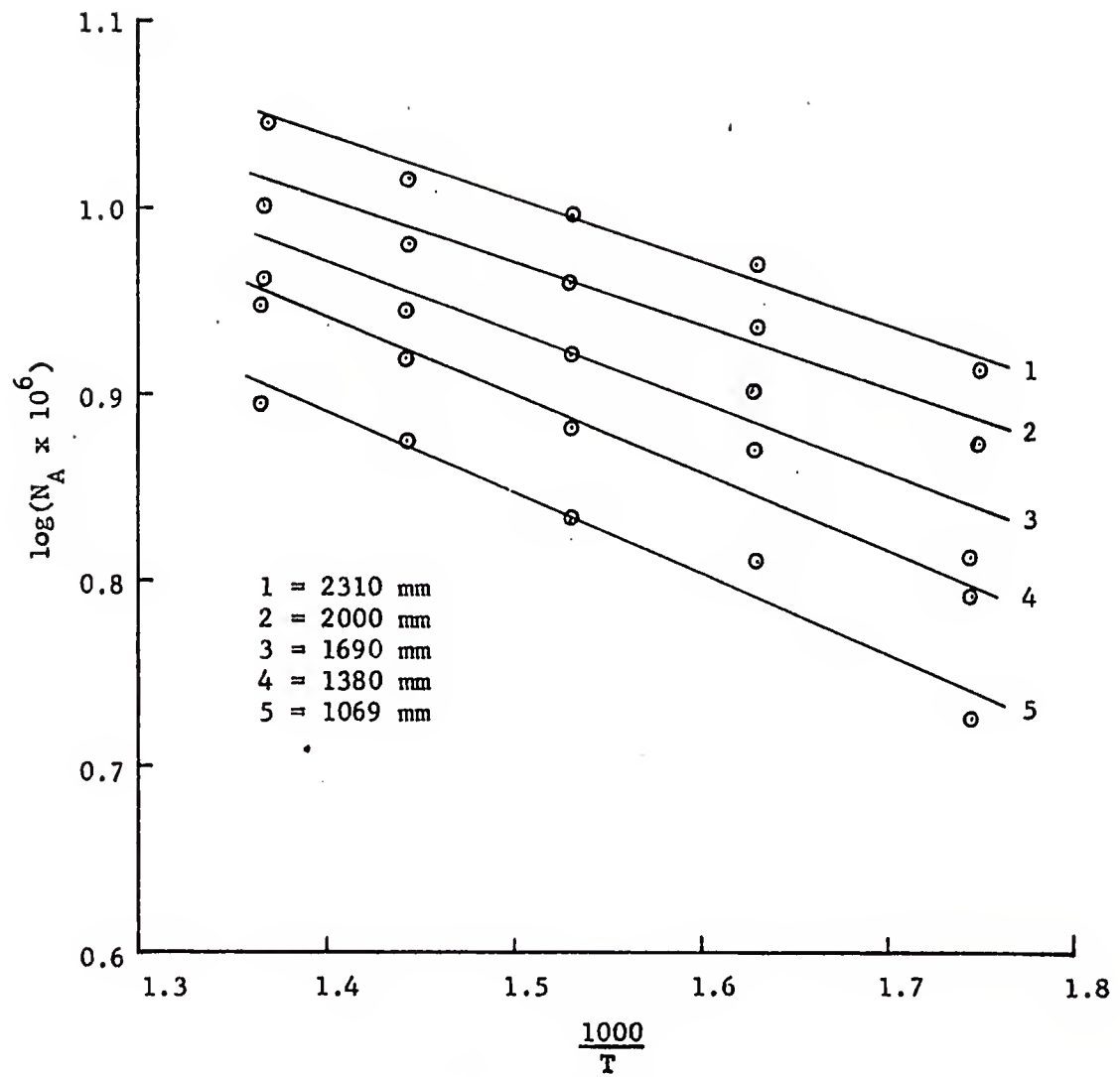


Figure 30. Determination of the Energy of Activation

B: 1.11×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

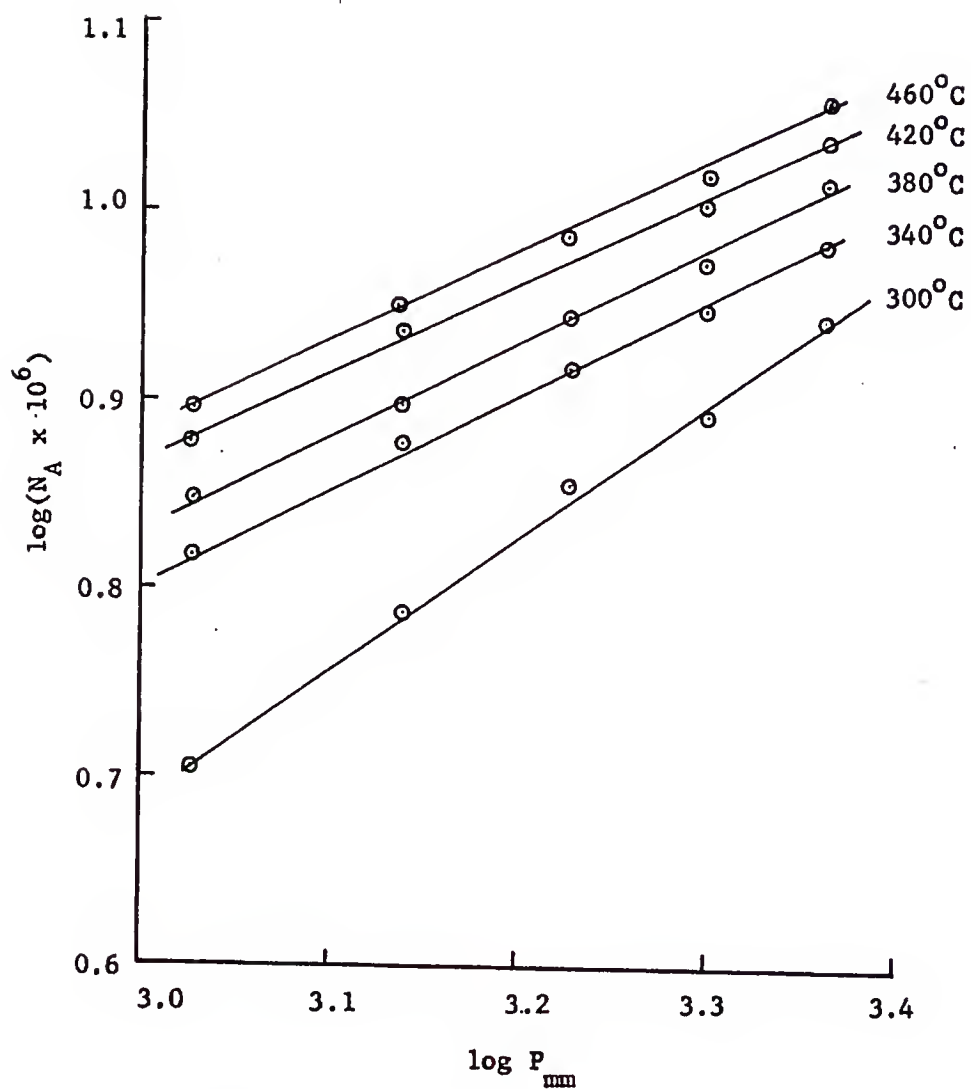


Figure 31. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

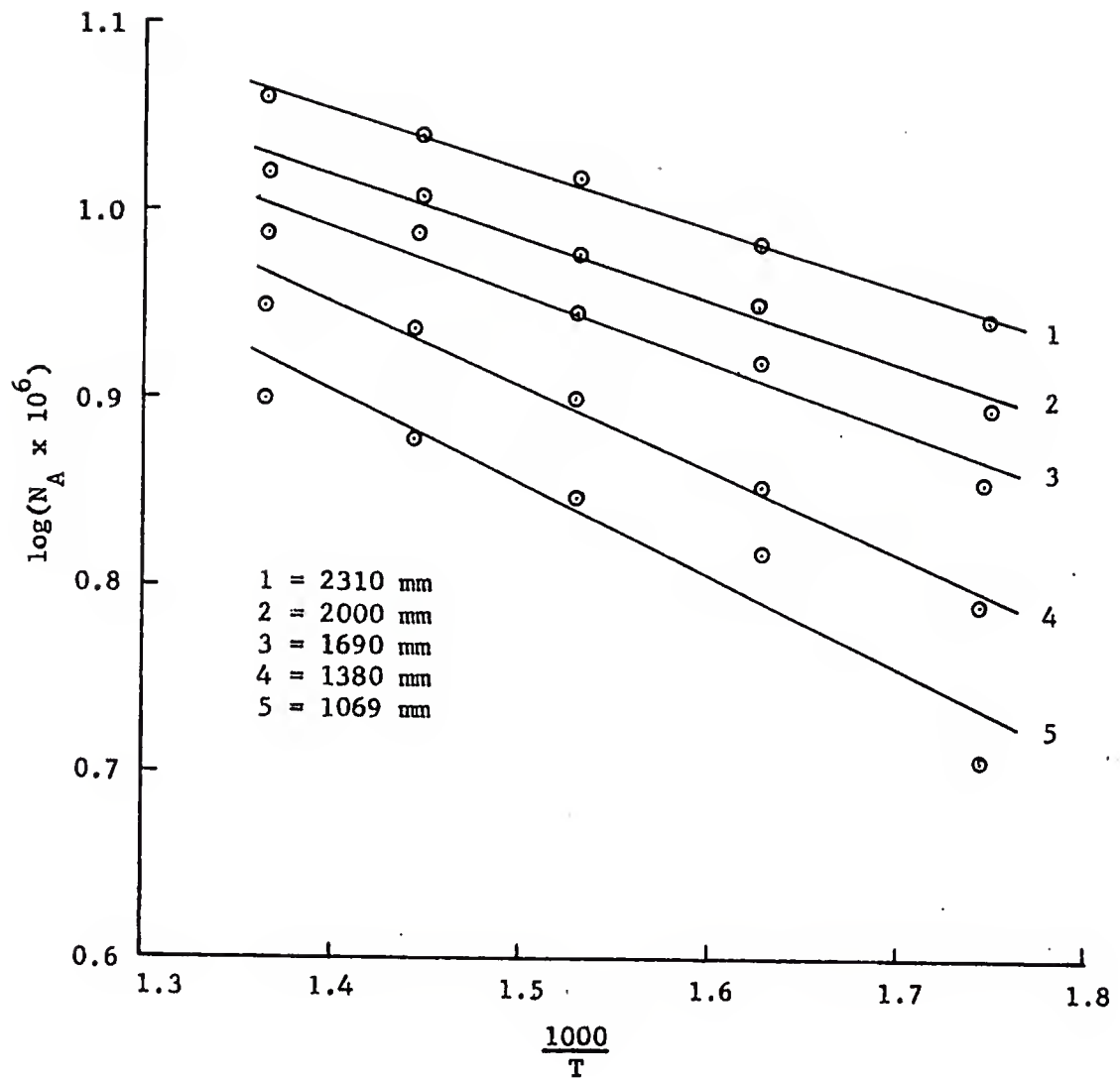


Figure 32. Determination of the Energy of Activation

B: 2.95×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

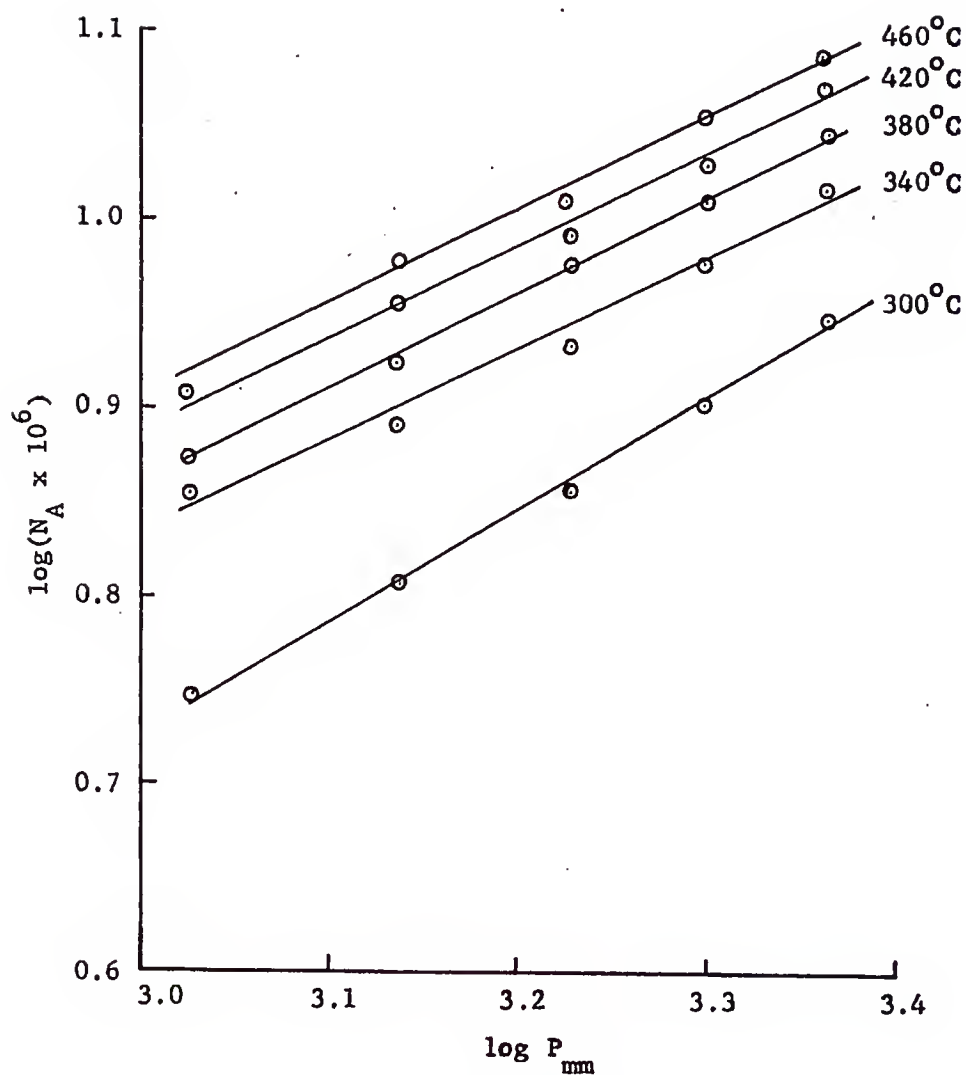


Figure 33. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

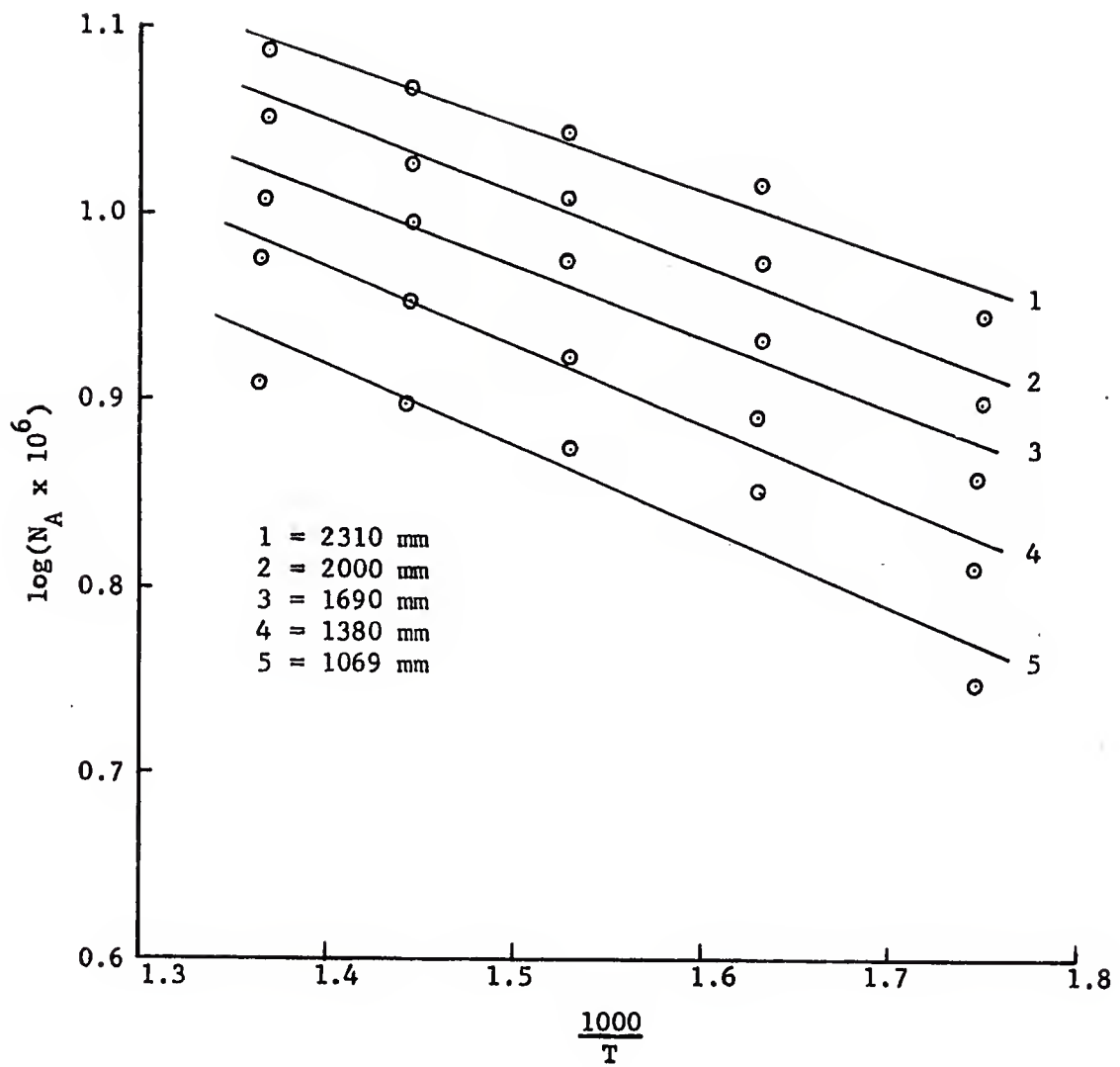


Figure 34. Determination of the Energy of Activation

B: 0.93×10^{-5} gm.mole/cm²sec.

Feed Gas Composition: 25.6% N₂, 74.4% H₂

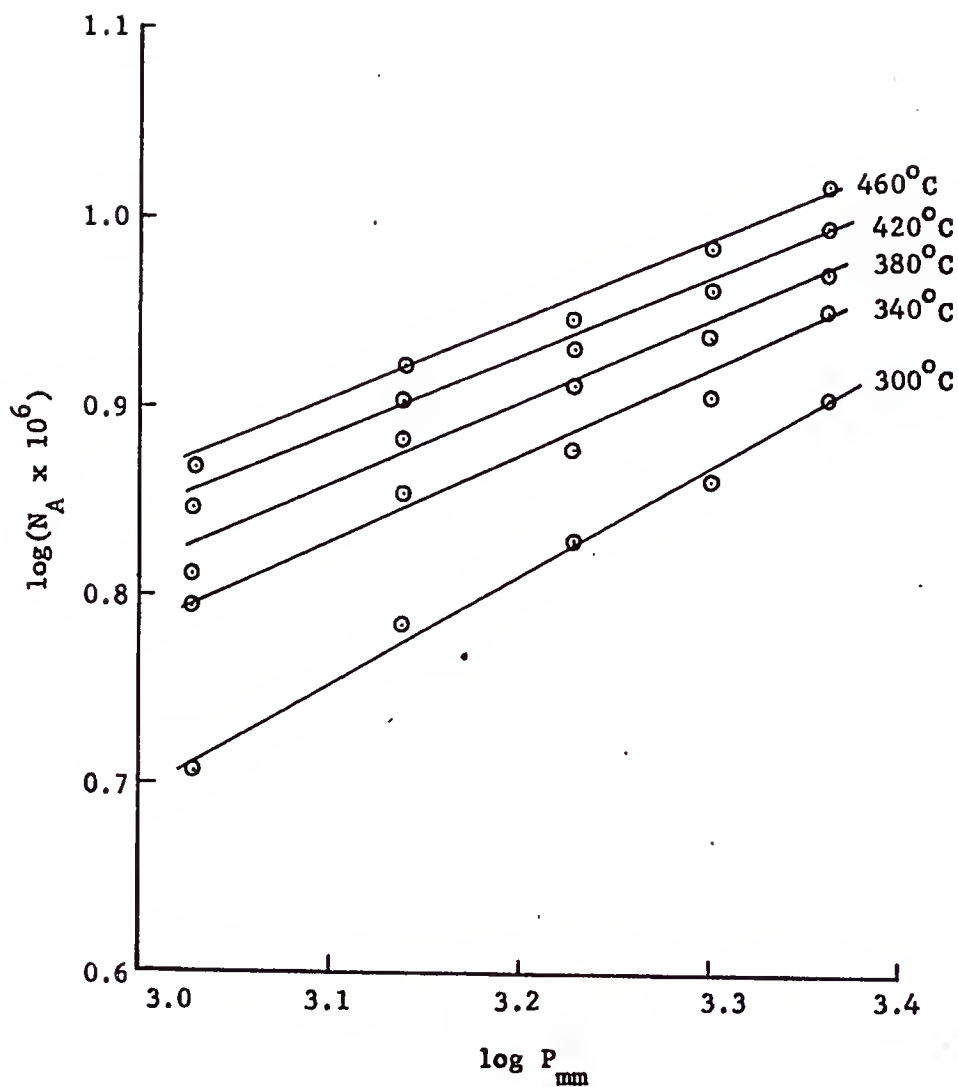


Figure 35. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

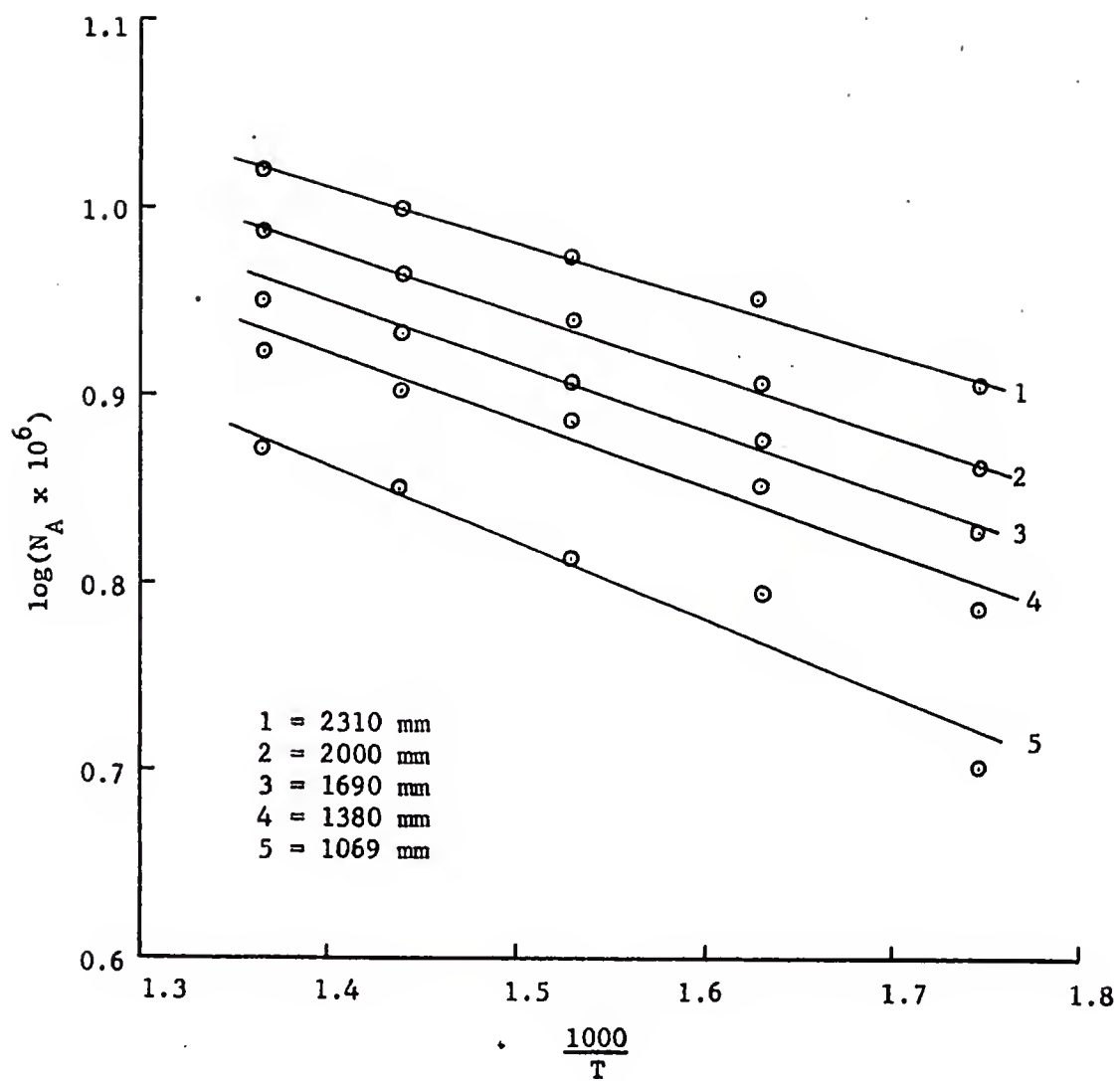


Figure 36. Determination of the Energy of Activation

B: 2.46×10^{-5} gm.molas/cm²sec.

Feed Gas Composition: 25.6% N₂, 74.4% H₂

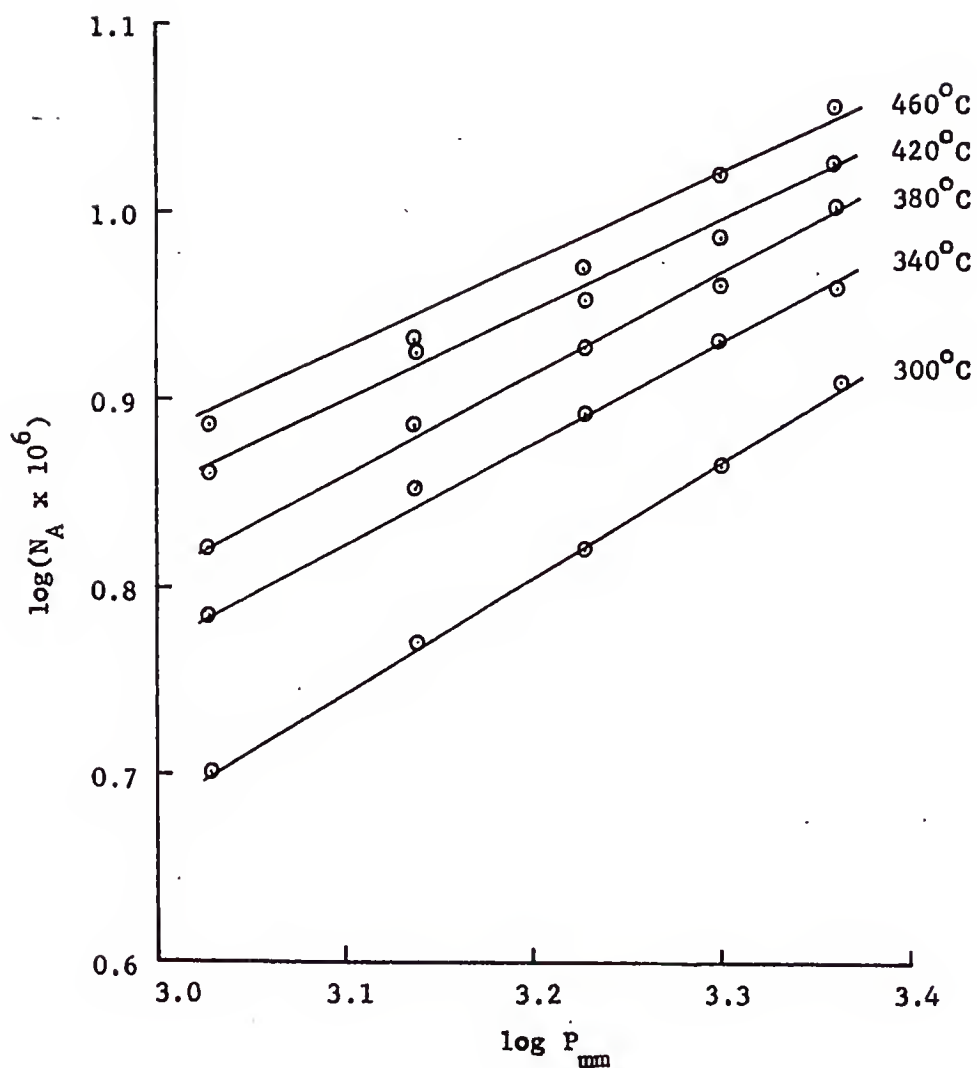


Figure 37. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

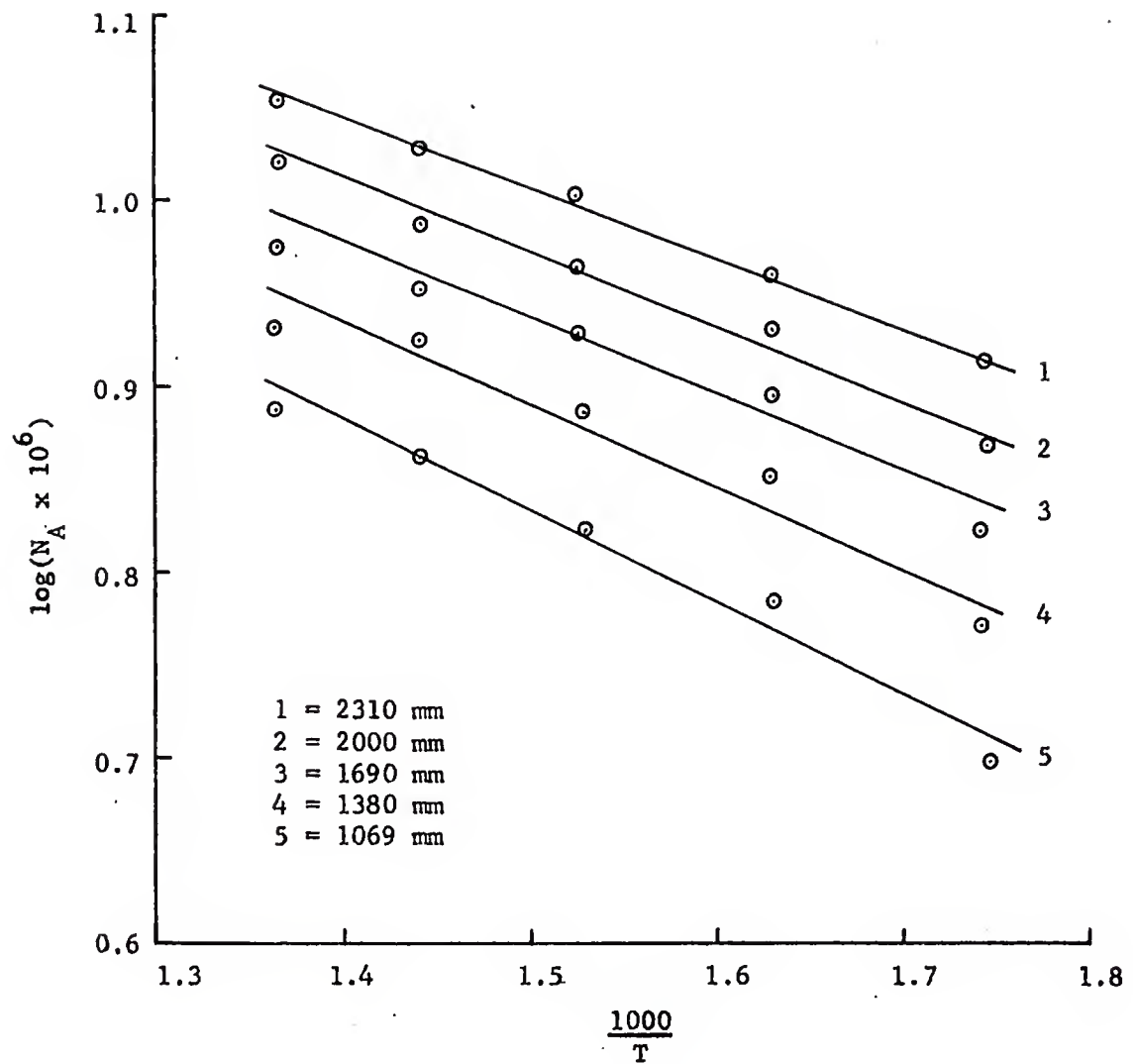


Figure 38. Determination of the Energy of Activation

B: 1.25×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

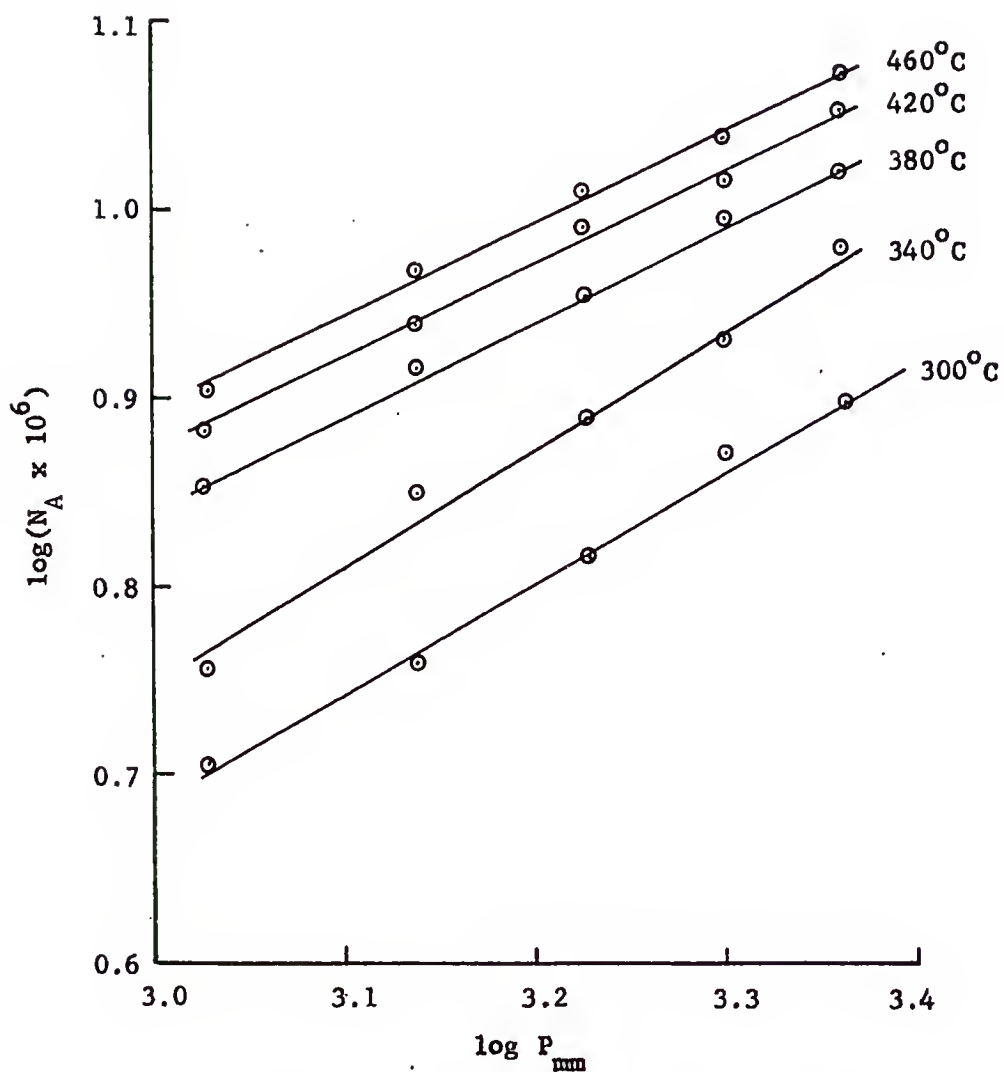


Figure 39. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

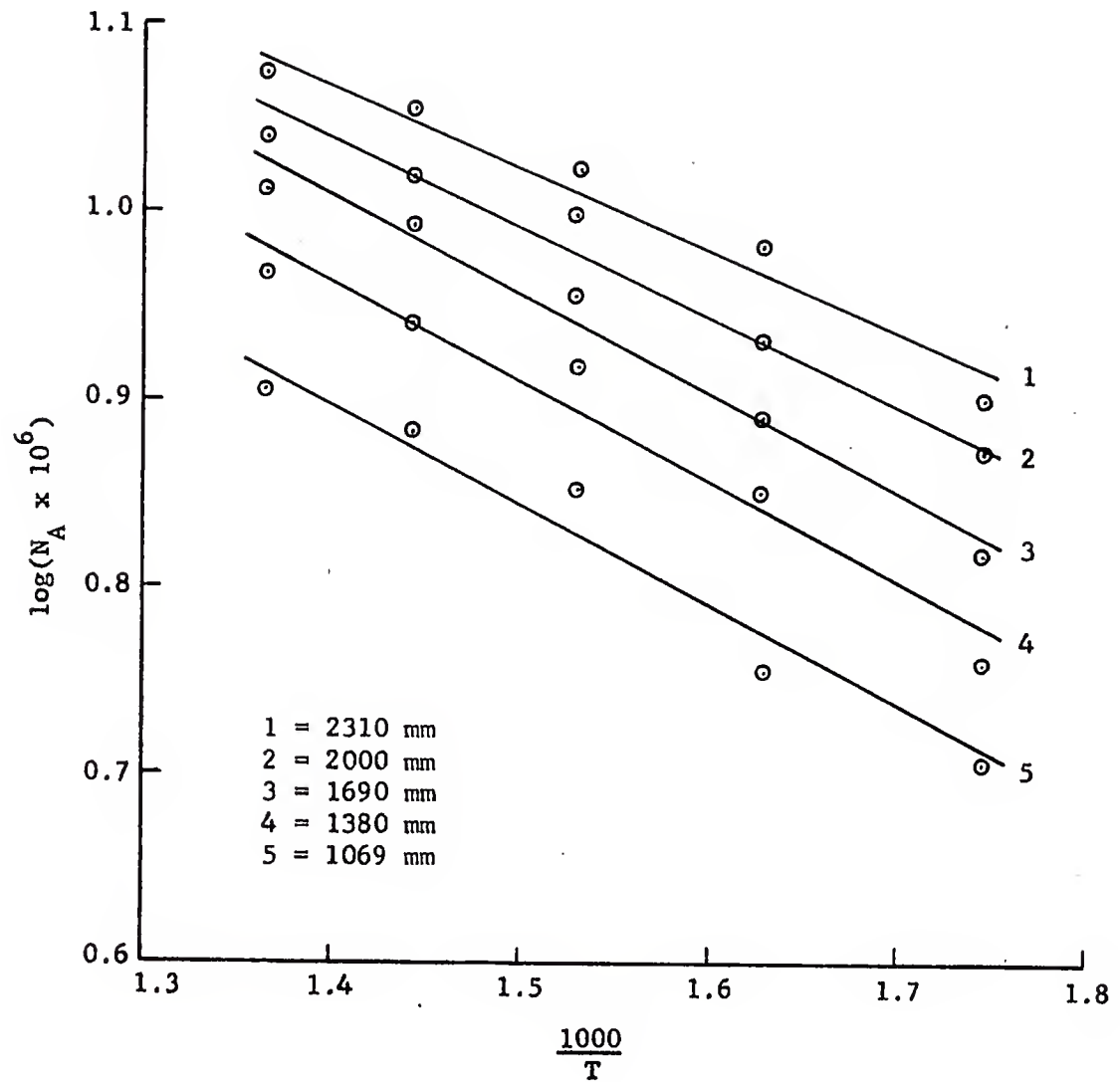


Figure 40. Determination of the Energy of Activation

B: 3.24×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

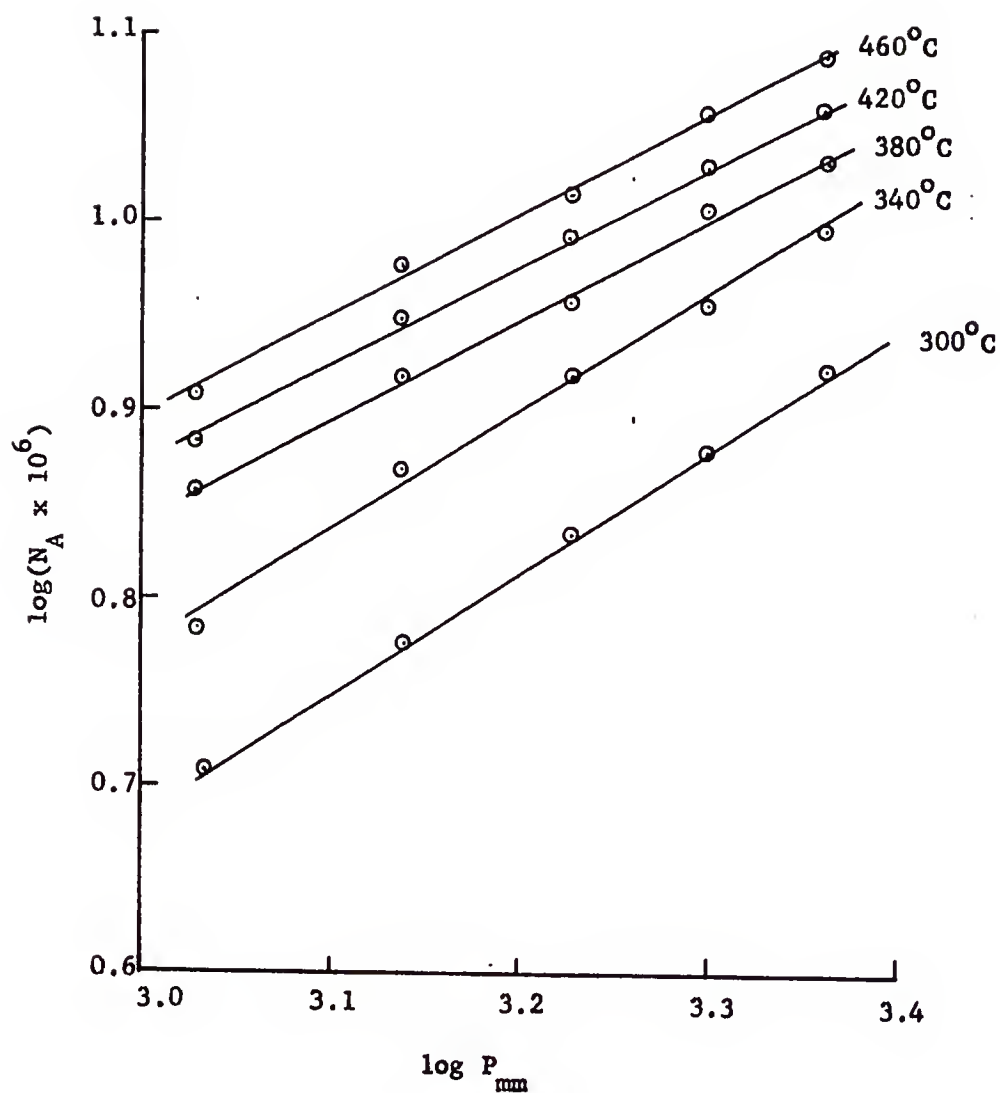


Figure 41. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

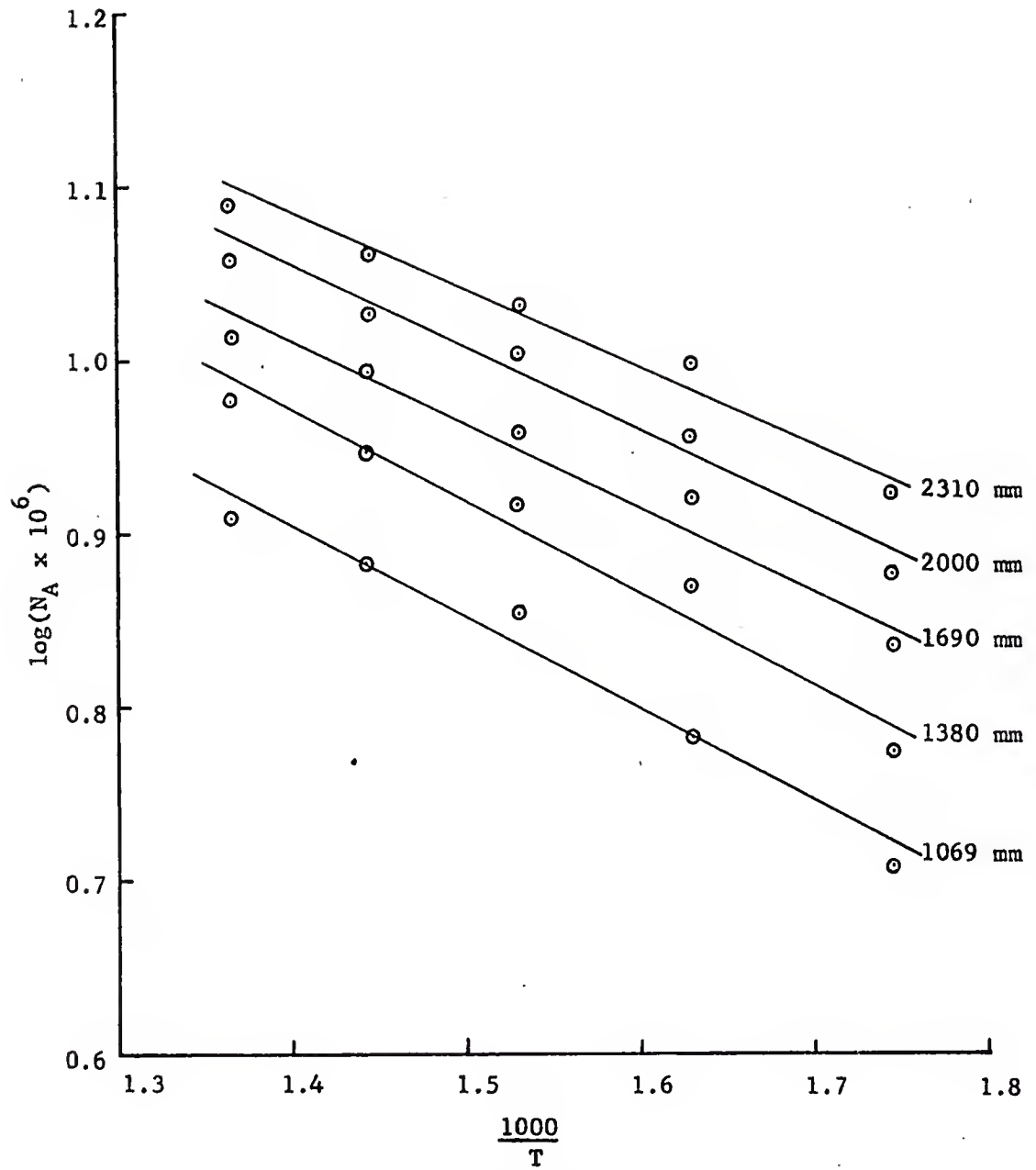


Figure 42. Determination of the Energy of Activation

B: 0.86×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

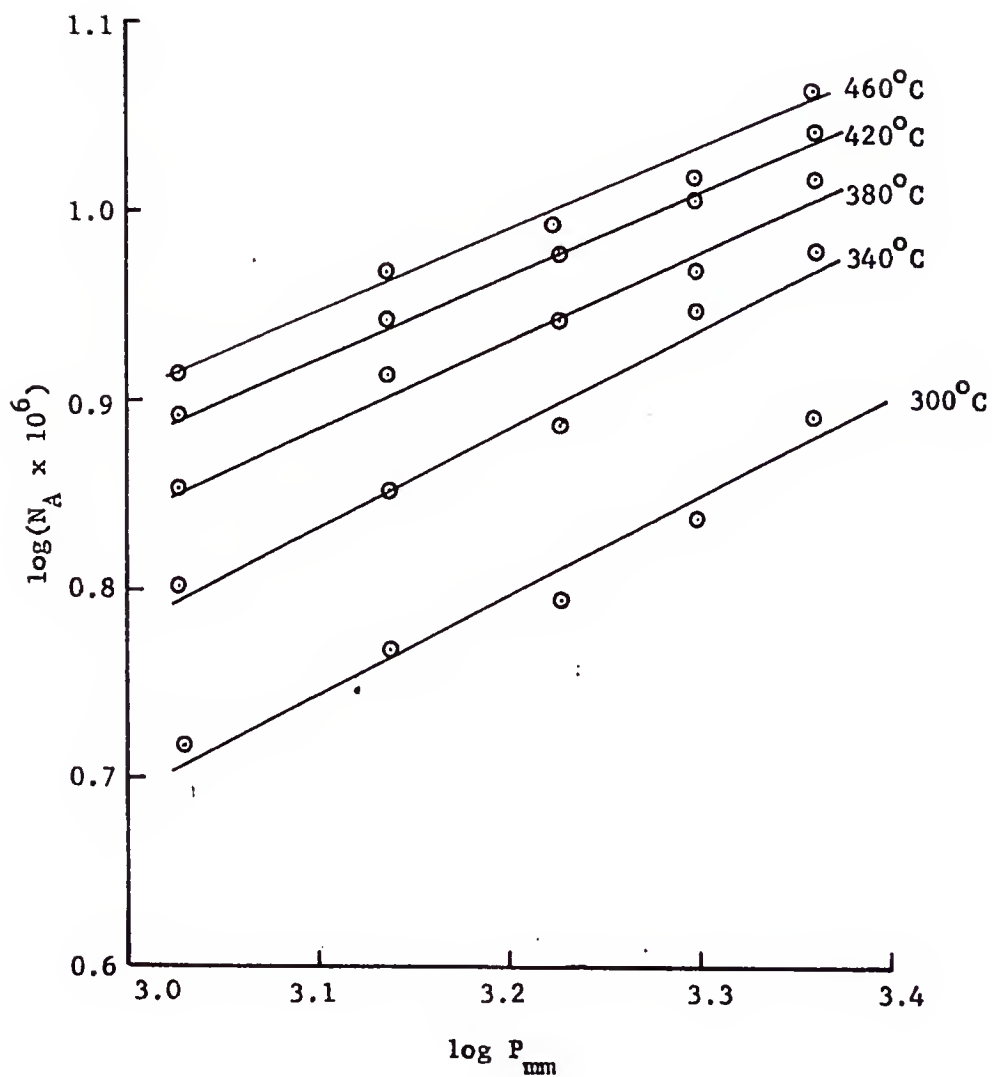


Figure 43. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane

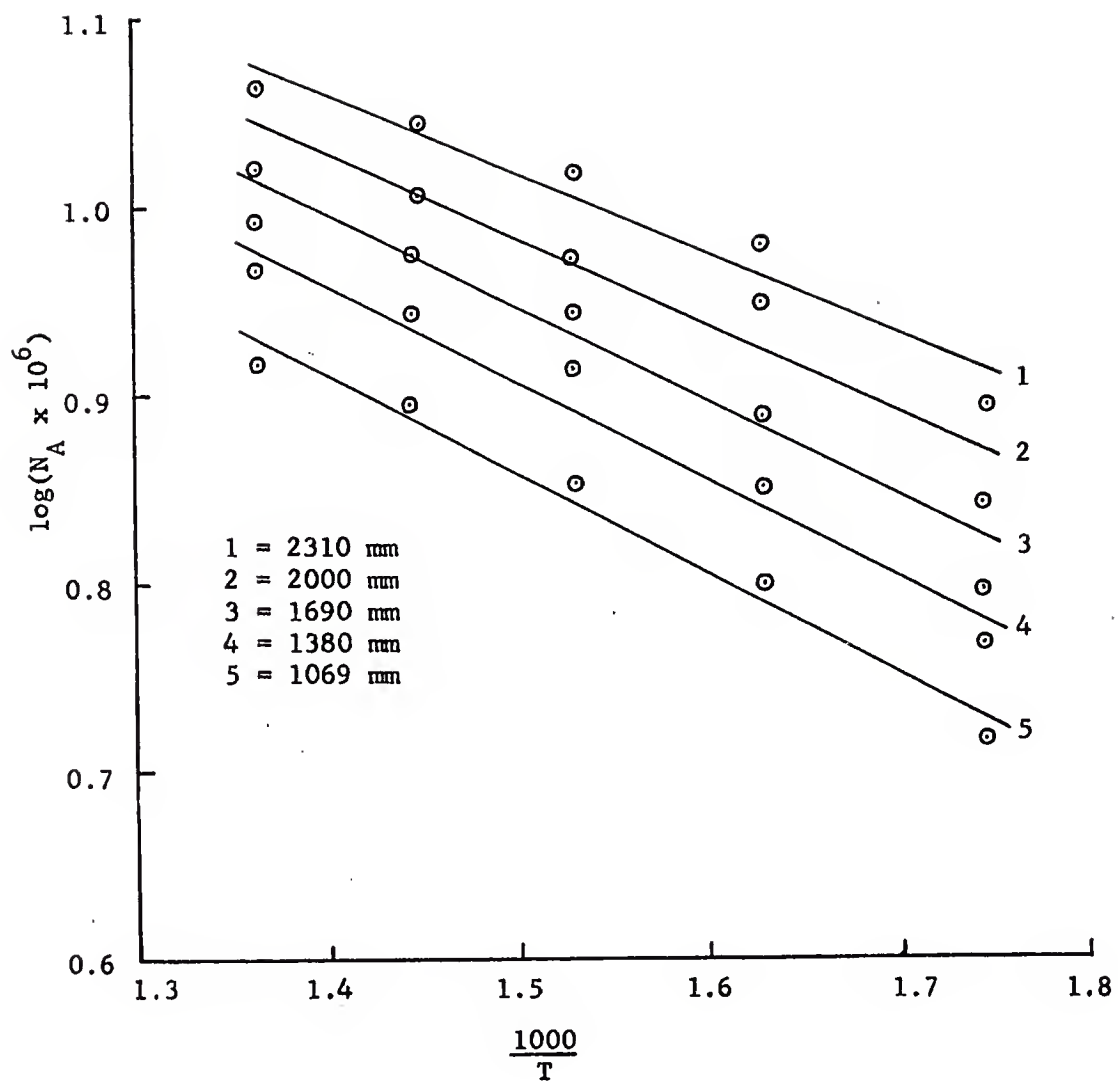


Figure 44. Determination of the Energy of Activation

B: 2.32×10^{-5} gm.moles/cm² sec.

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

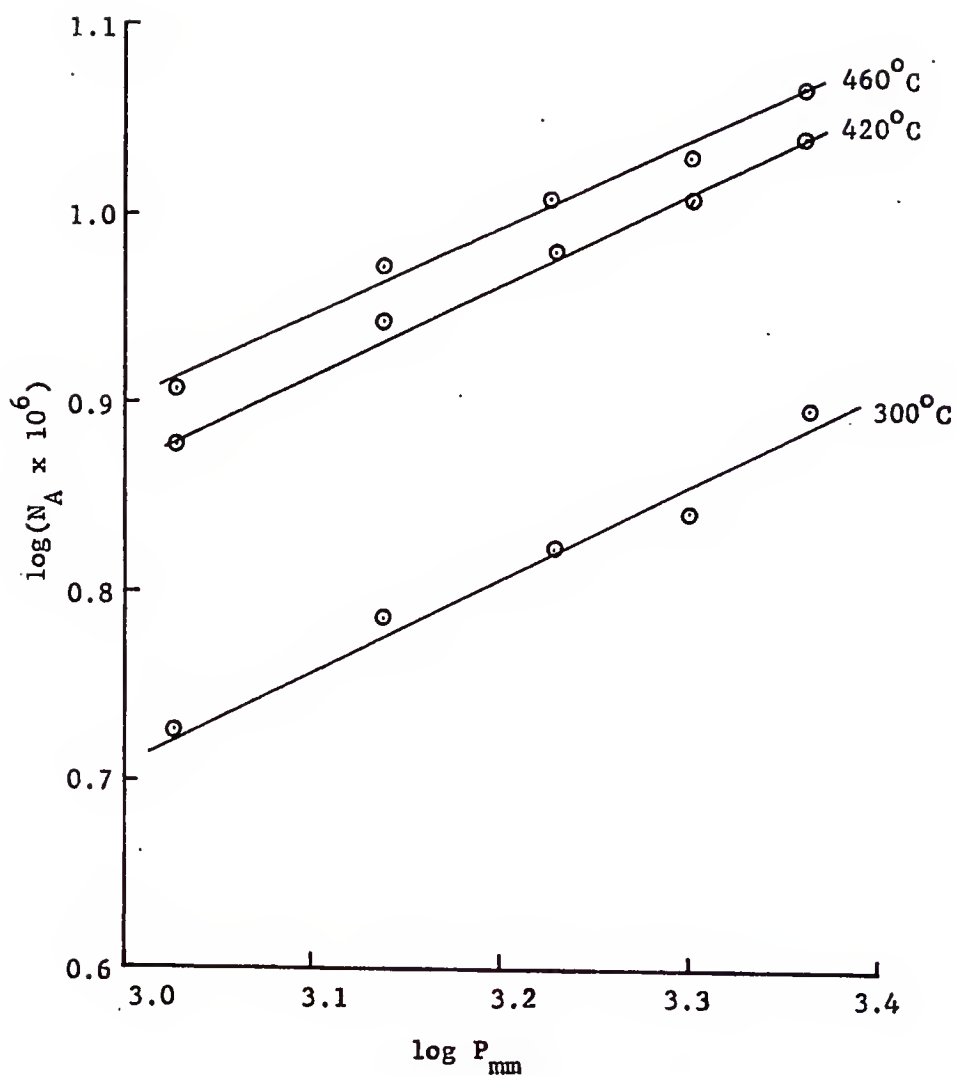


Figure 45. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane

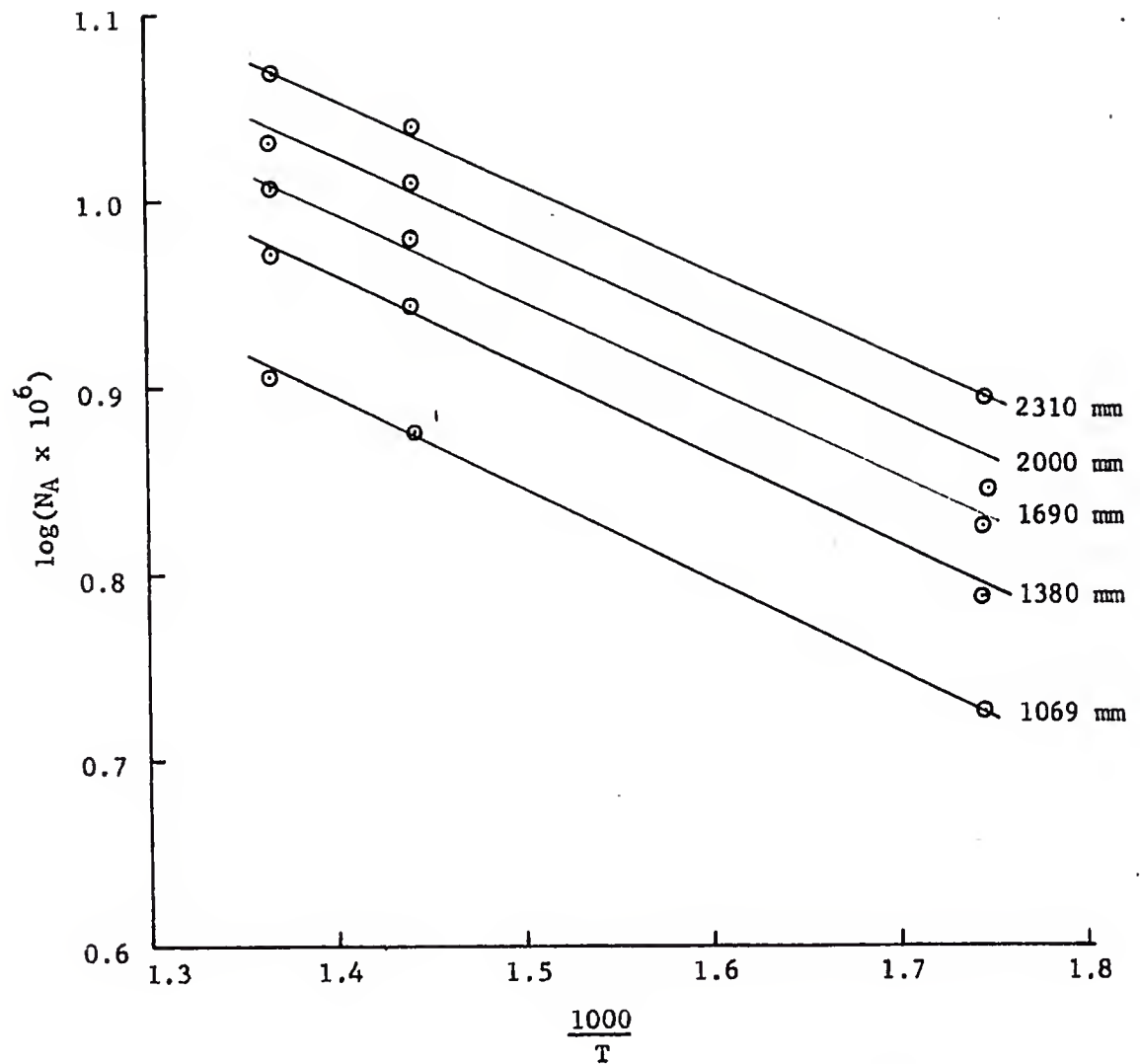


Figure 46. Determination of the Energy of Activation

B: 0.99×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 21% CO₂, 79% H₂

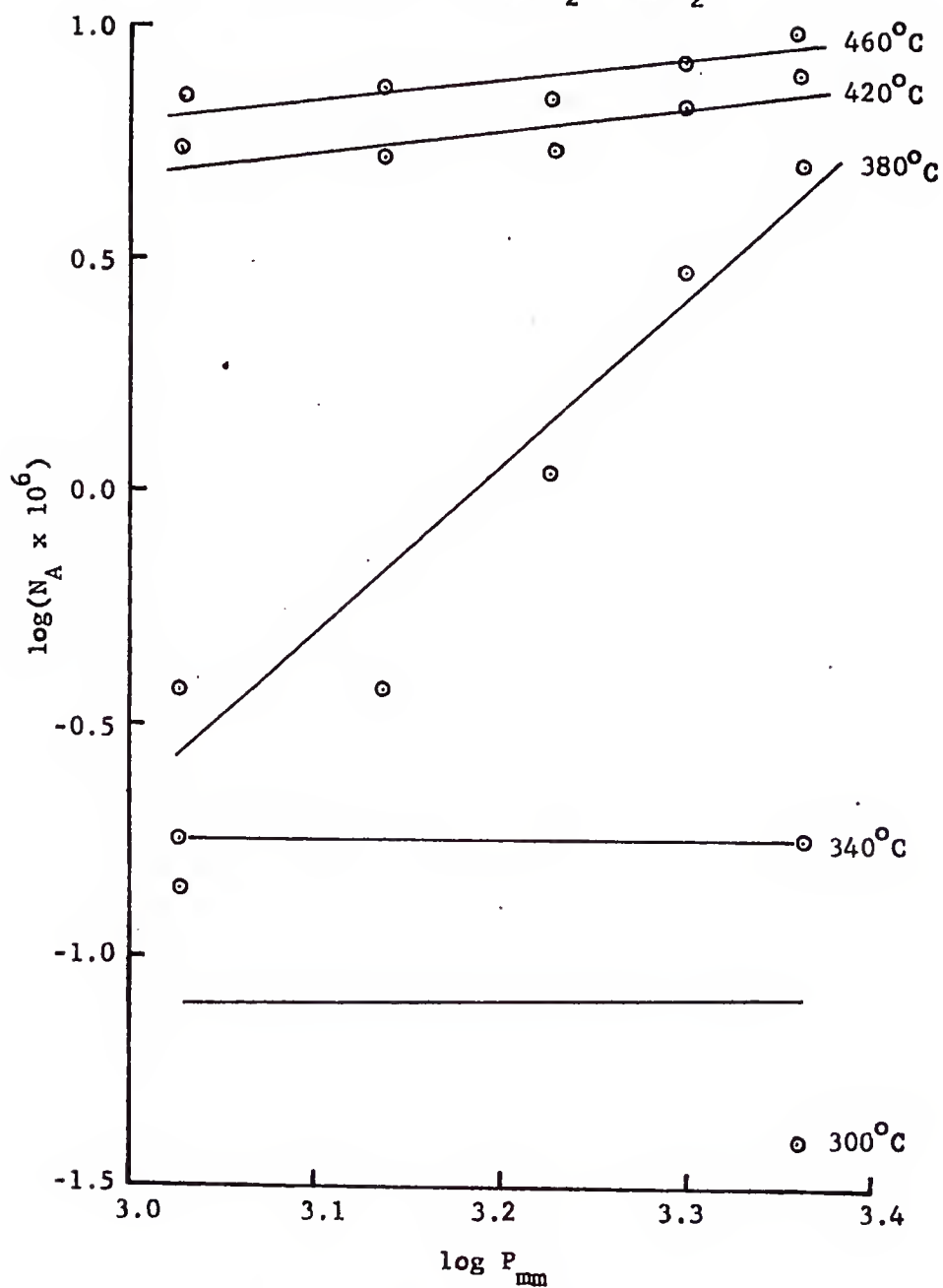


Figure 47. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane

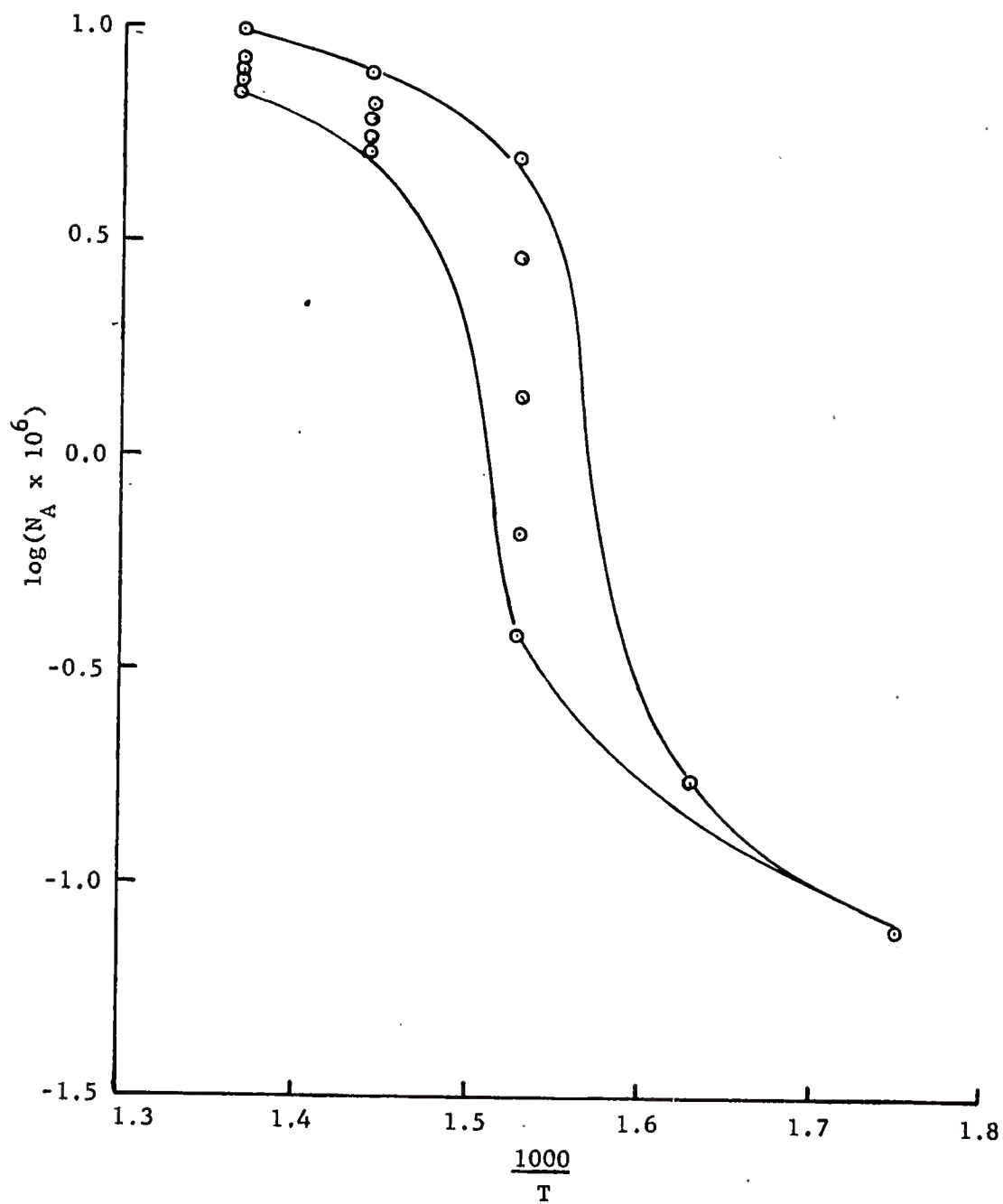


Figure 48. Determination of the Energy of Activation

B: 2.52×10^{-5} gm.moles/cm²sec.

Feed Gas Composition: 21% CO, 79% H₂

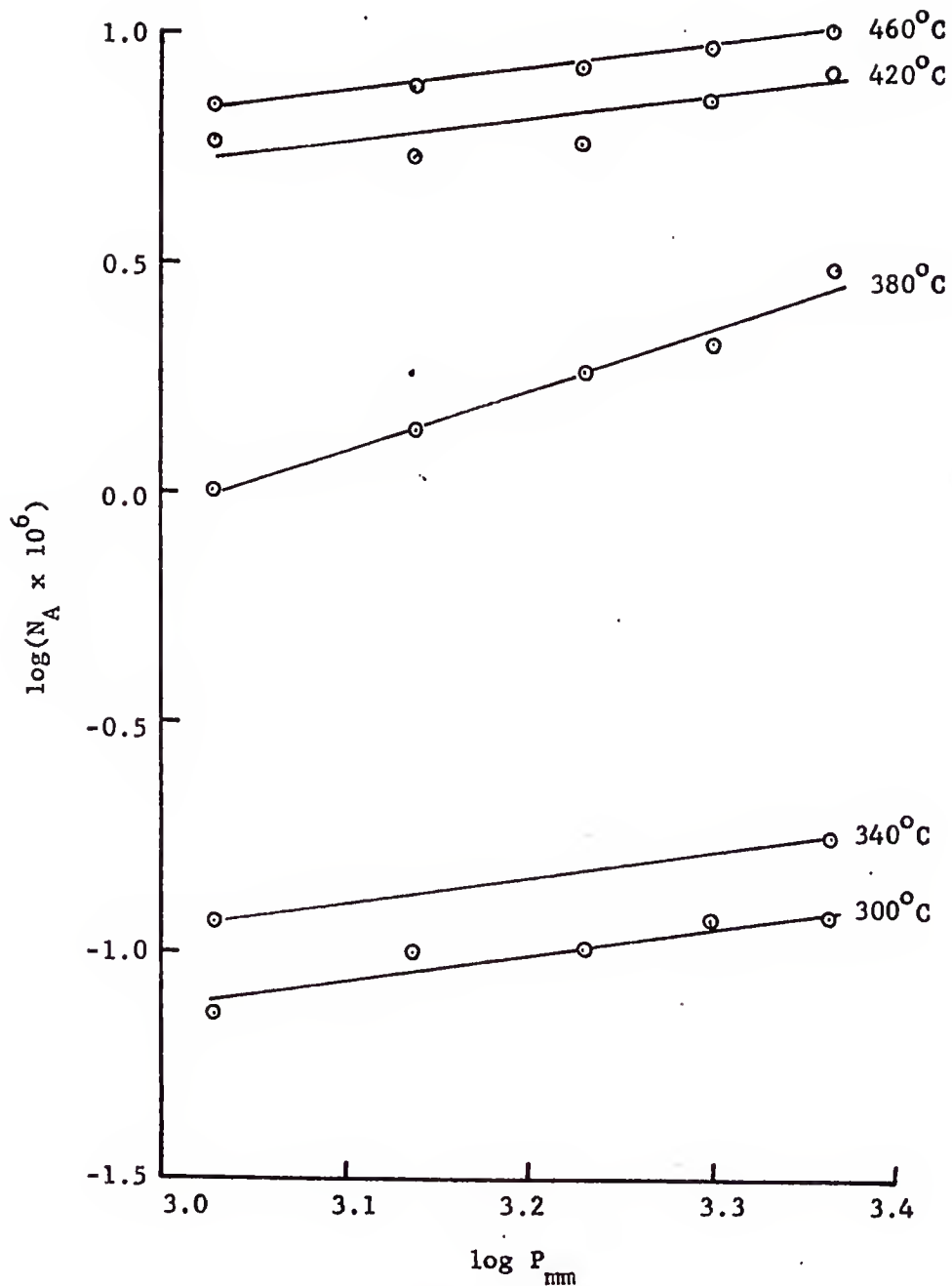


Figure 49. Effect of Impurities on the Rate of Transport of H₂ Through Pd-Ag Membrane

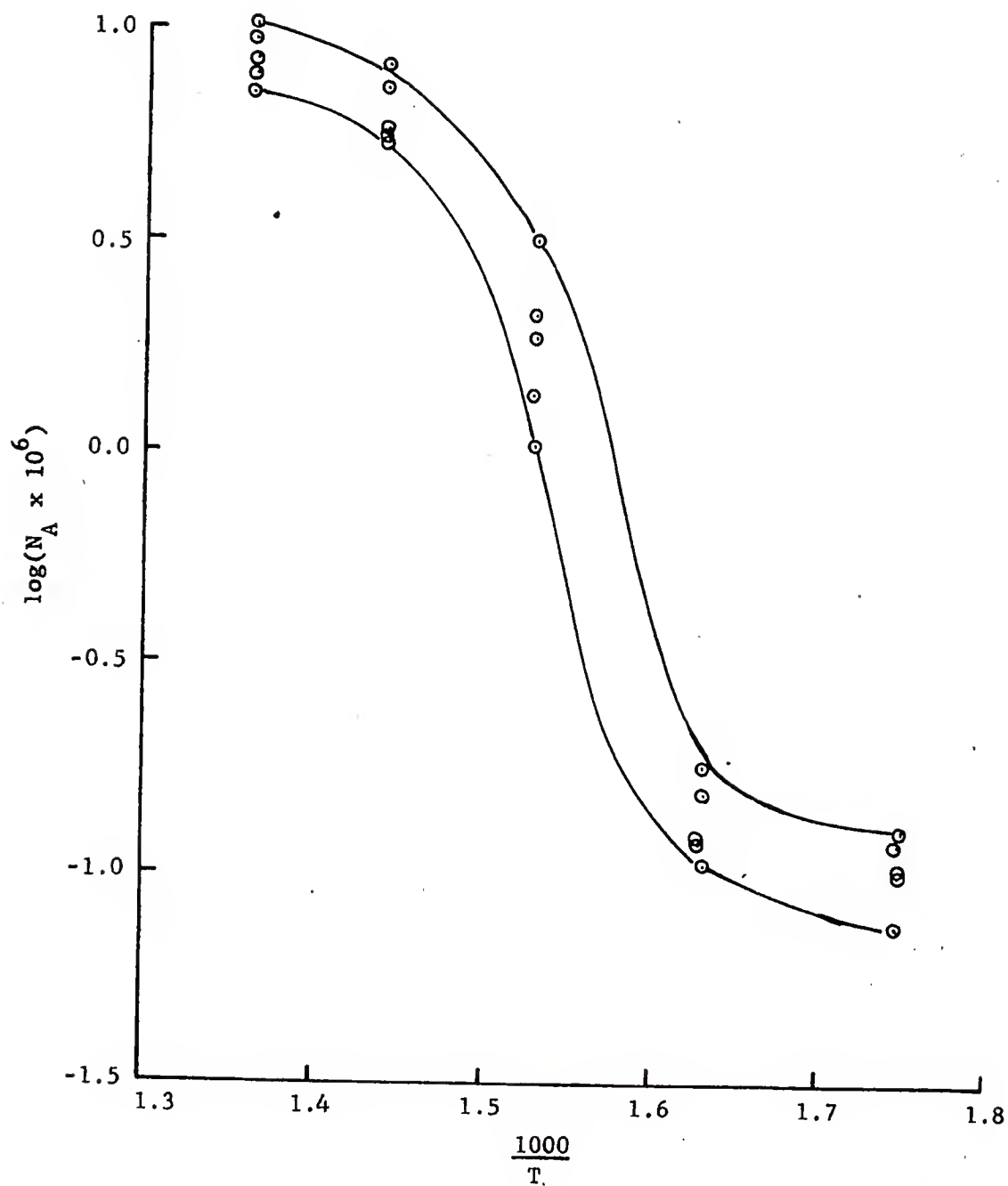


Figure 50. Determination of the Energy of Activation

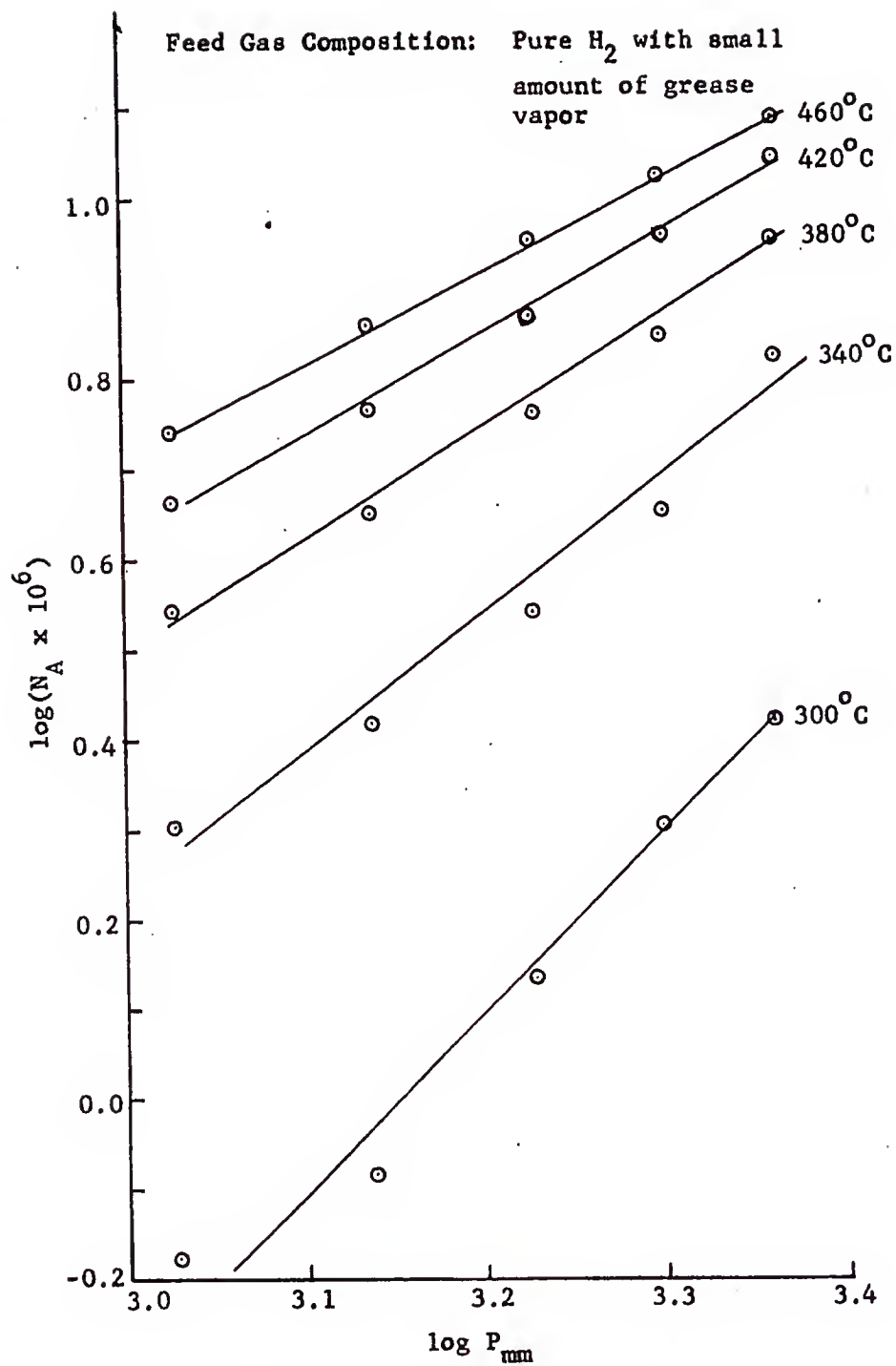


Figure 51. Effect of Impurities on the Rate of Transport of H_2 Through Pd-Ag Membrane at Different Temperatures

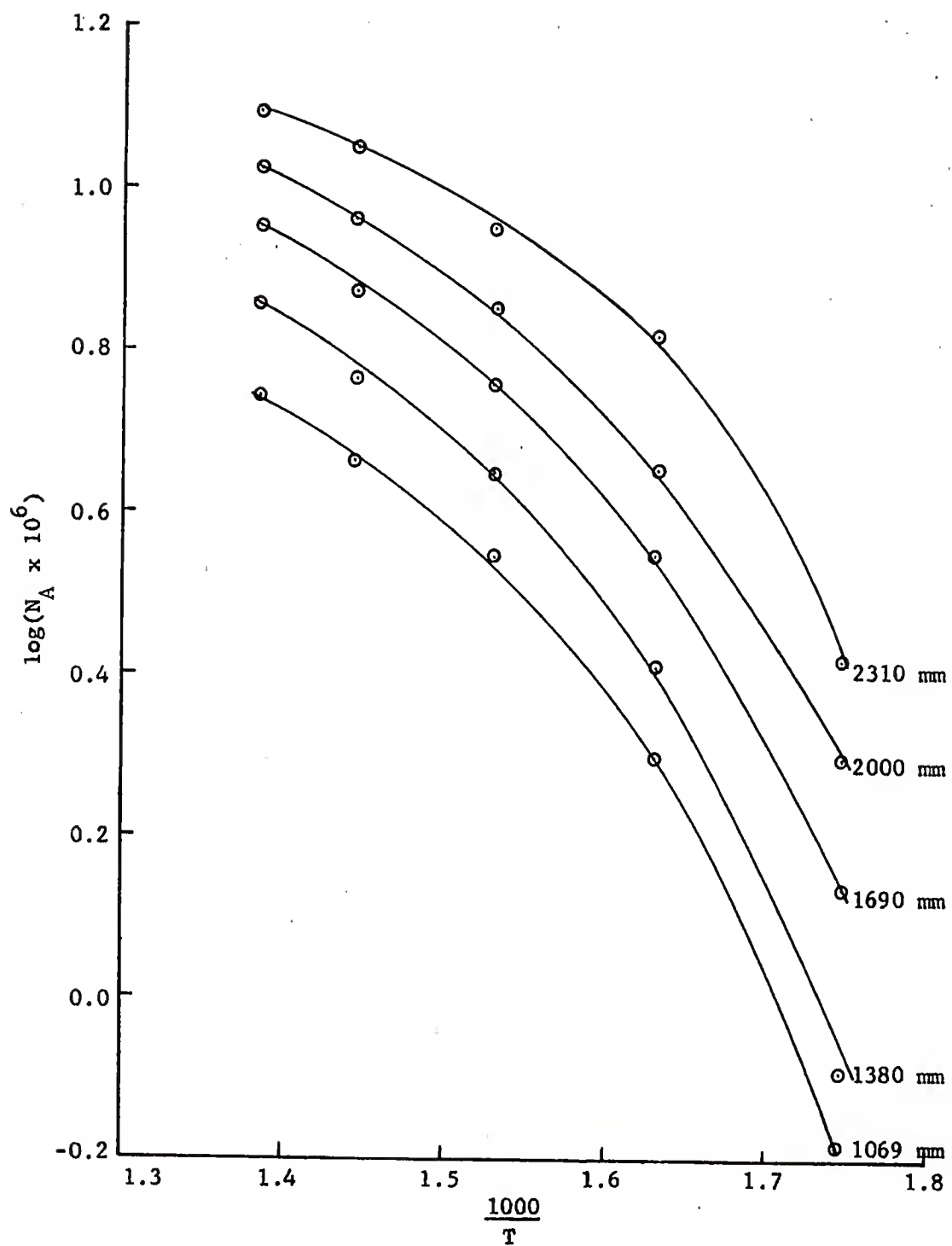


Figure 52. Determination of the Energy of Activation

TABLE 22

MULTIPLE REGRESSION OF THE CONSTANTS IN EQUATION (108)

Feed Gas Composition	Bleed Rate B gm.moles/cm ² sec.	k_1	k_1'	$\frac{1}{n}$	$\frac{\Delta E}{R}$
30% CH ₄ , 10% N ₂ , 60% H ₂	0.55 x 10 ⁻⁵	3.5 x 10 ⁻⁶	2.9 x 10 ⁻⁶	0.38	-1490
	1.08 x 10 ⁻⁵	1.7 x 10 ⁻⁶	1.3 x 10 ⁻⁷	0.48	-1430
	1.88 x 10 ⁻⁵	1.1 x 10 ⁻⁶	8.5 x 10 ⁻⁷	0.51	-1280
	2.80 x 10 ⁻⁵	1.2 x 10 ⁻⁶	9.1 x 10 ⁻⁷	0.49	-1200
10% CH ₄ , 10% N ₂ , 80% H ₂	0.38 x 10 ⁻⁵	7.7 x 10 ⁻⁷	6.9 x 10 ⁻⁷	0.45	-680
	0.52 x 10 ⁻⁵	9.3 x 10 ⁻⁷	8.4 x 10 ⁻⁷	0.46	-810
	1.11 x 10 ⁻⁵	6.9 x 10 ⁻⁷	6.1 x 10 ⁻⁷	0.52	-870
	2.95 x 10 ⁻⁵	7.5 x 10 ⁻⁷	6.7 x 10 ⁻⁷	0.52	-900
25.6% N ₂ , 74.4% H ₂	0.93 x 10 ⁻⁵	8.1 x 10 ⁻⁷	7.1 x 10 ⁻⁷	0.47	-770
	2.46 x 10 ⁻⁵	6.6 x 10 ⁻⁷	5.6 x 10 ⁻⁷	0.53	-930
19.8% CH ₄ , 80.2% H ₂	1.25 x 10 ⁻⁵	8.5 x 10 ⁻⁷	7.5 x 10 ⁻⁷	0.55	-1160
	3.24 x 10 ⁻⁵	7.9 x 10 ⁻⁷	7.0 x 10 ⁻⁷	0.56	-1100
21.5% CO ₂ , 78.5% H ₂	0.86 x 10 ⁻⁵	1.4 x 10 ⁻⁶	1.3 x 10 ⁻⁶	0.47	-1120
	2.32 x 10 ⁻⁵	1.3 x 10 ⁻⁶	1.1 x 10 ⁻⁶	0.48	-1080
100% H ₂ with Grease	NONE	3.3 x 10 ⁻⁷		1.35	-4790

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Temperature: 300°C

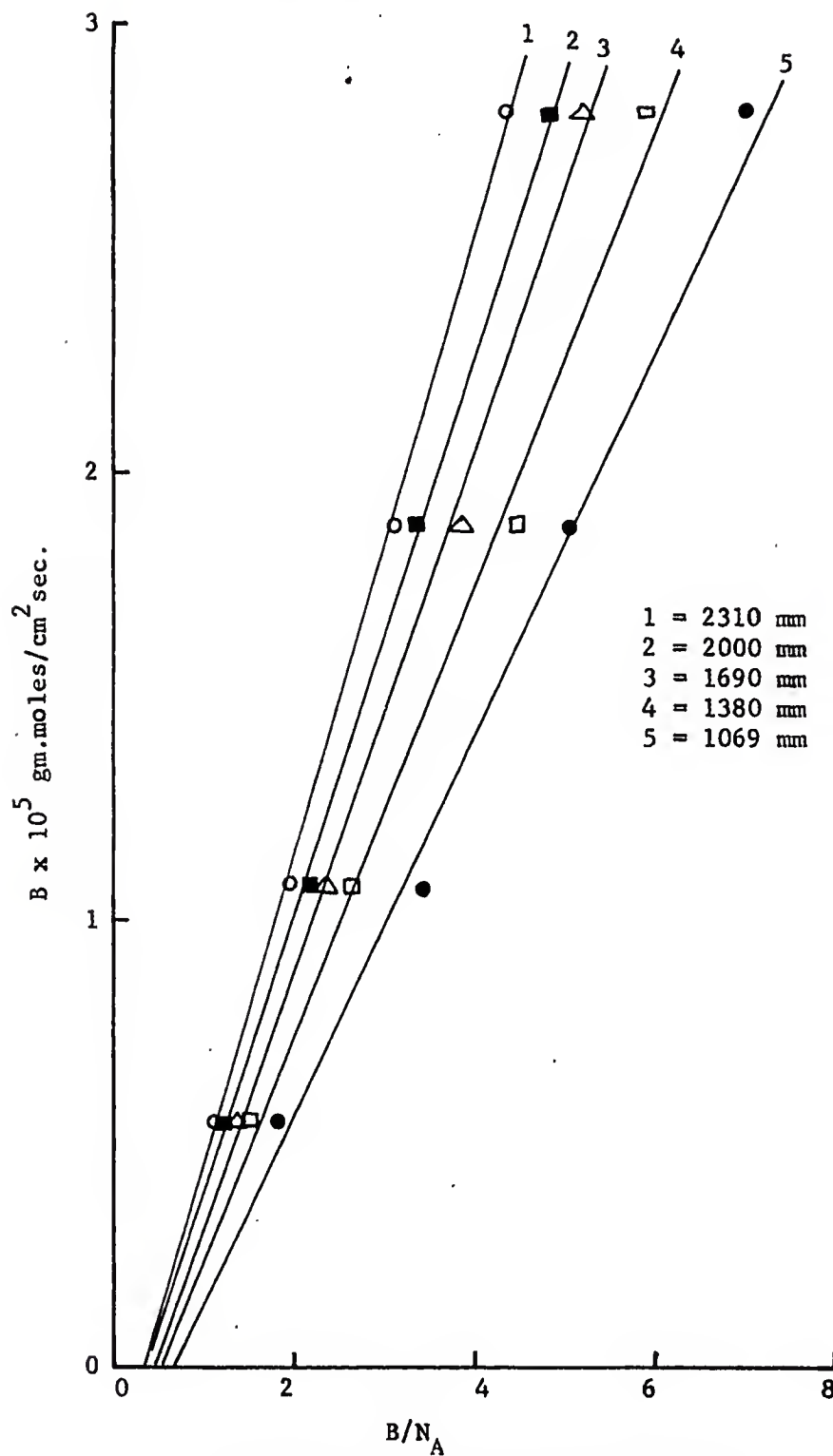
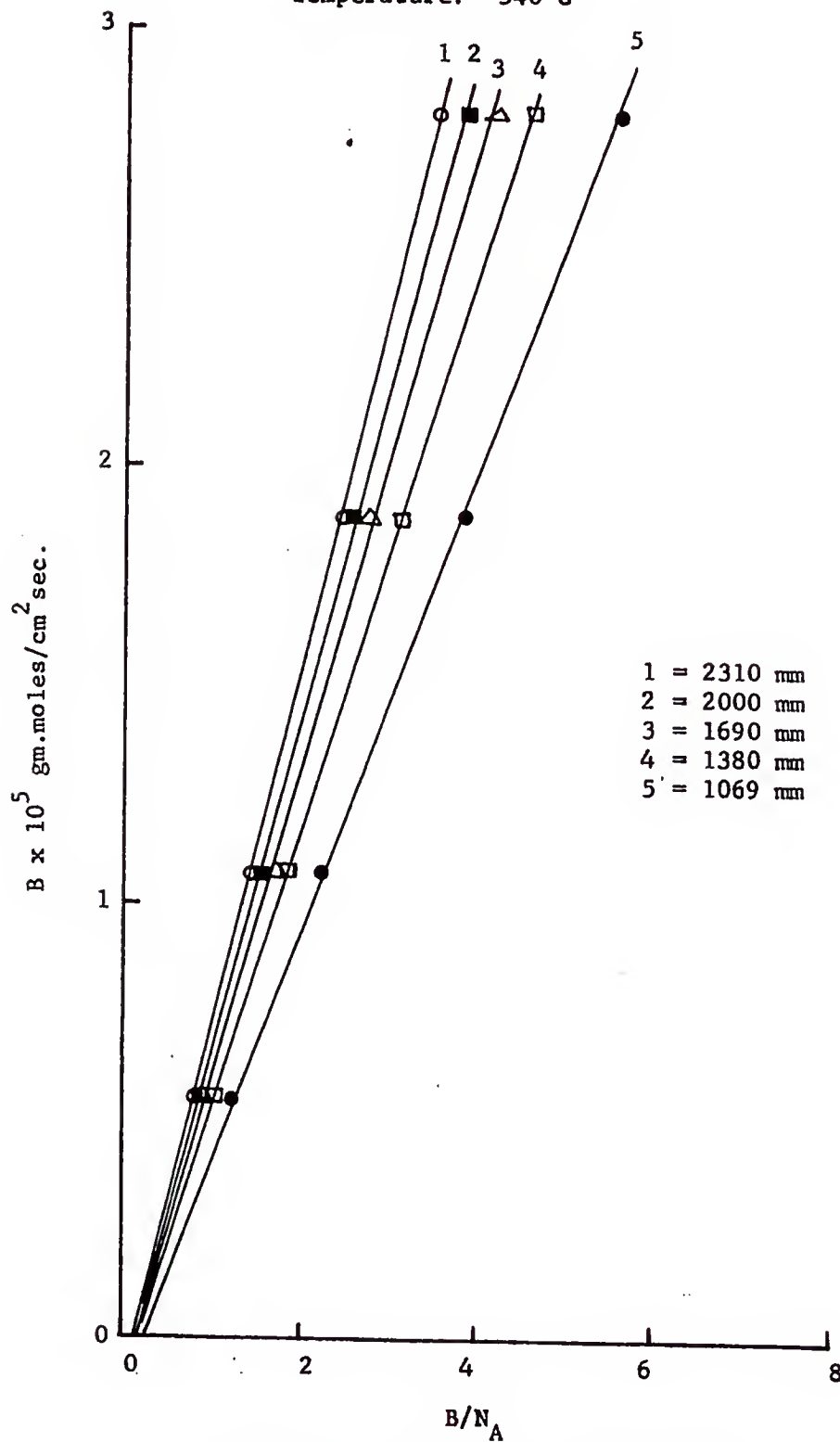


Figure 53. A Plot of B Versus B/N_A

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Temperature: 340°C

Figure 54. A Plot of B Versus B/N_A

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Temperature: 380°C

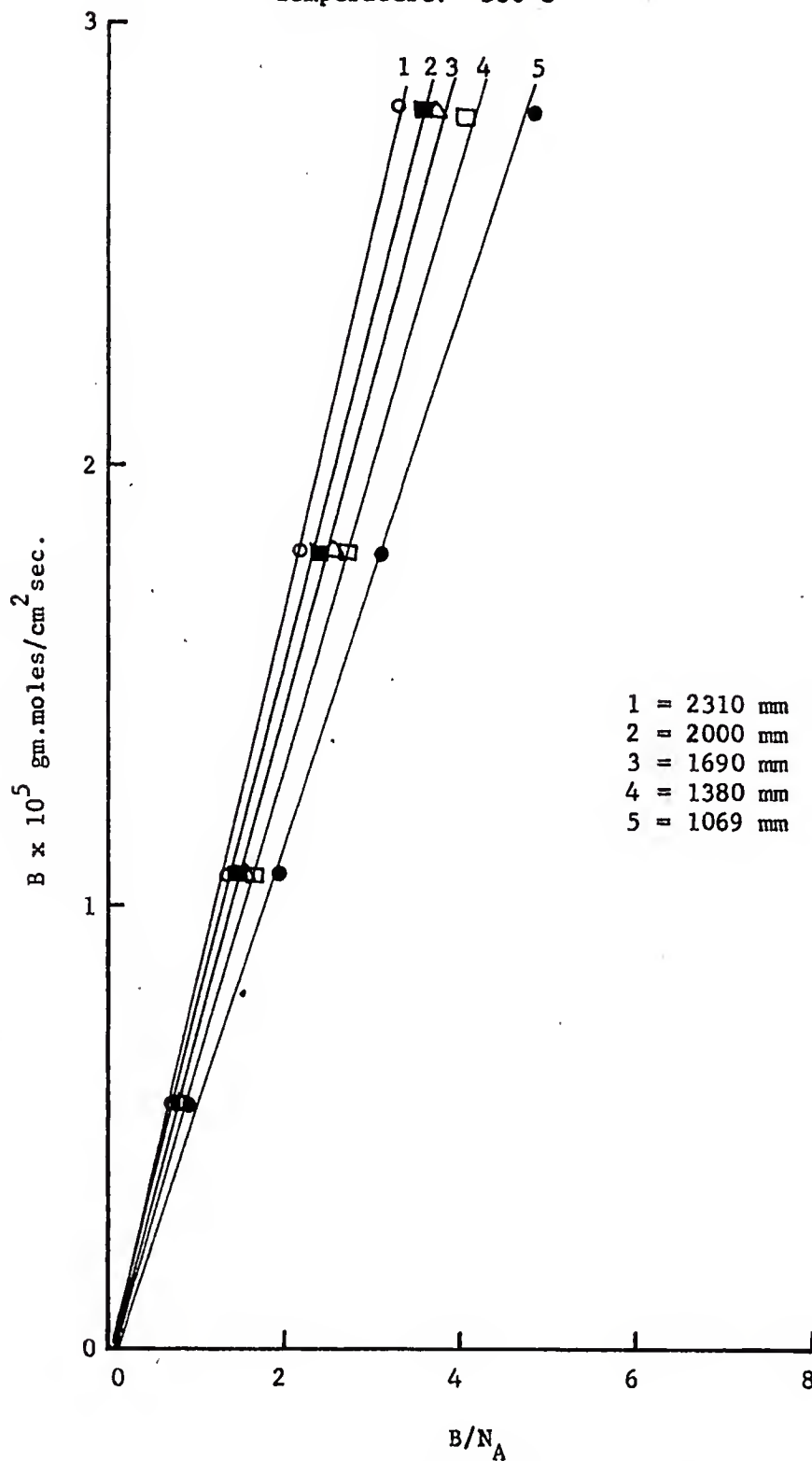


Figure 55. A Plot of B Versus B/N_A

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Temperature: 420°C

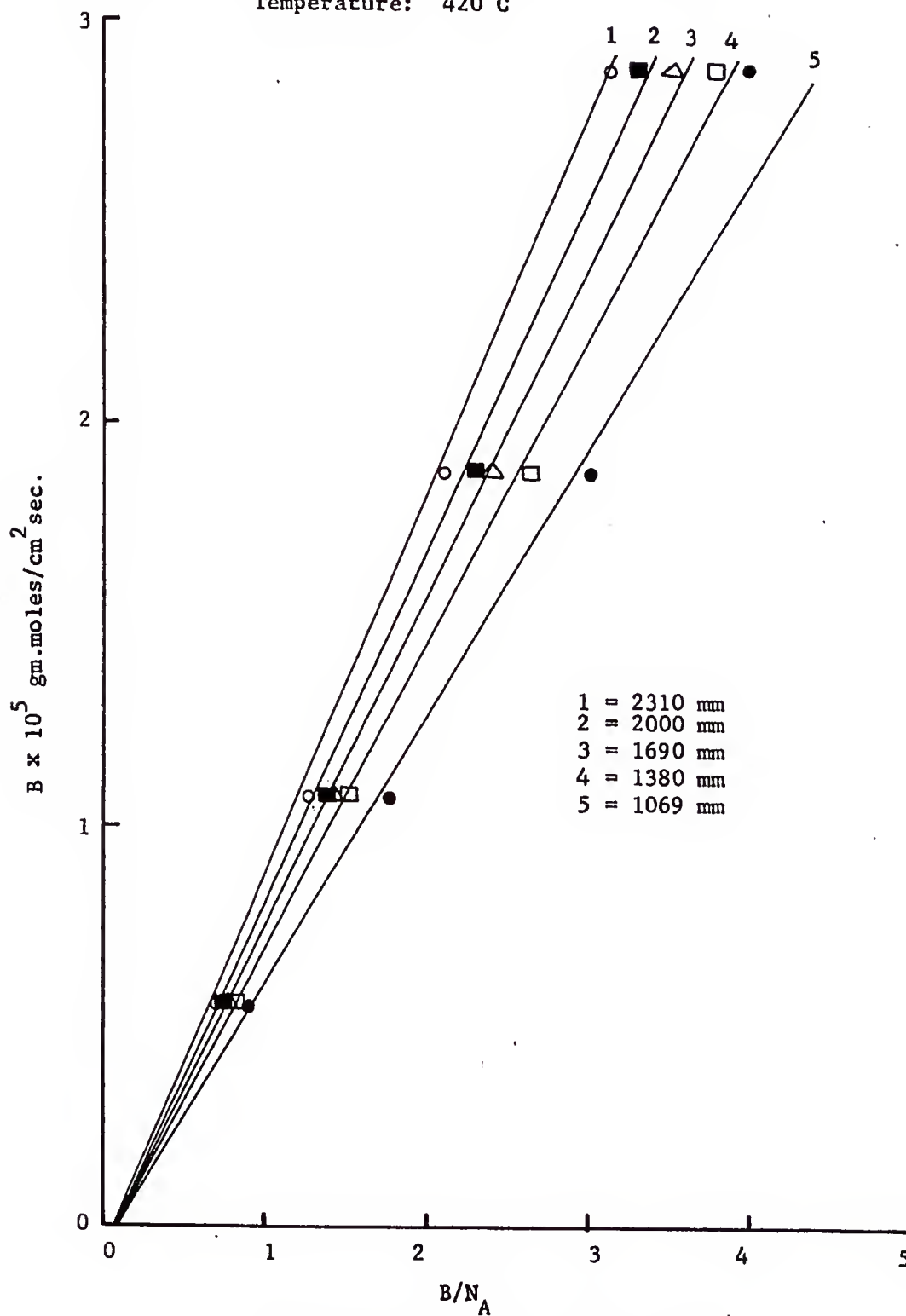


Figure 56. A Plot of B Versus B/N_A

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

Temperature: 460°C

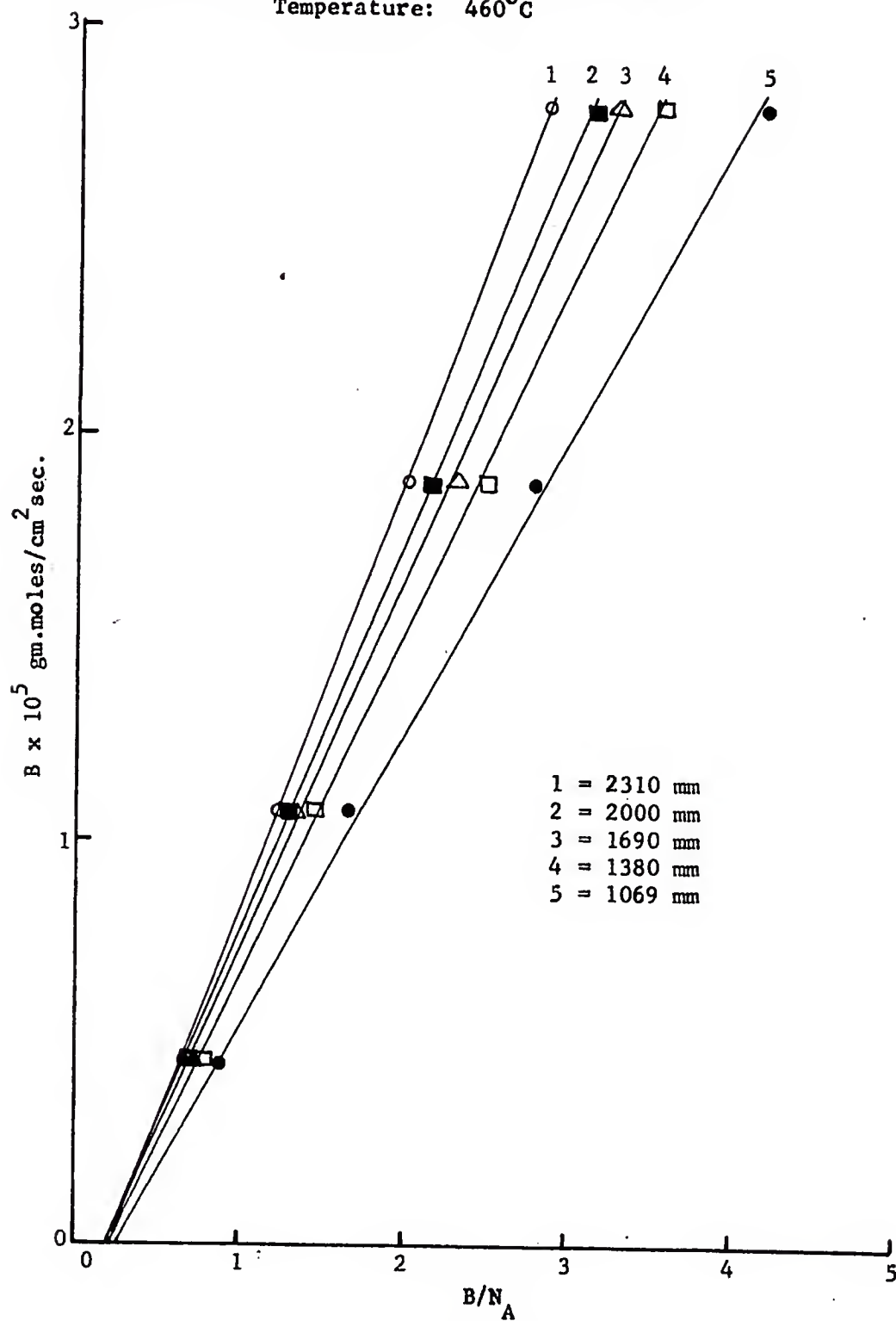


Figure 57. A Plot of B Versus B/N_A

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Temperature: 300°C

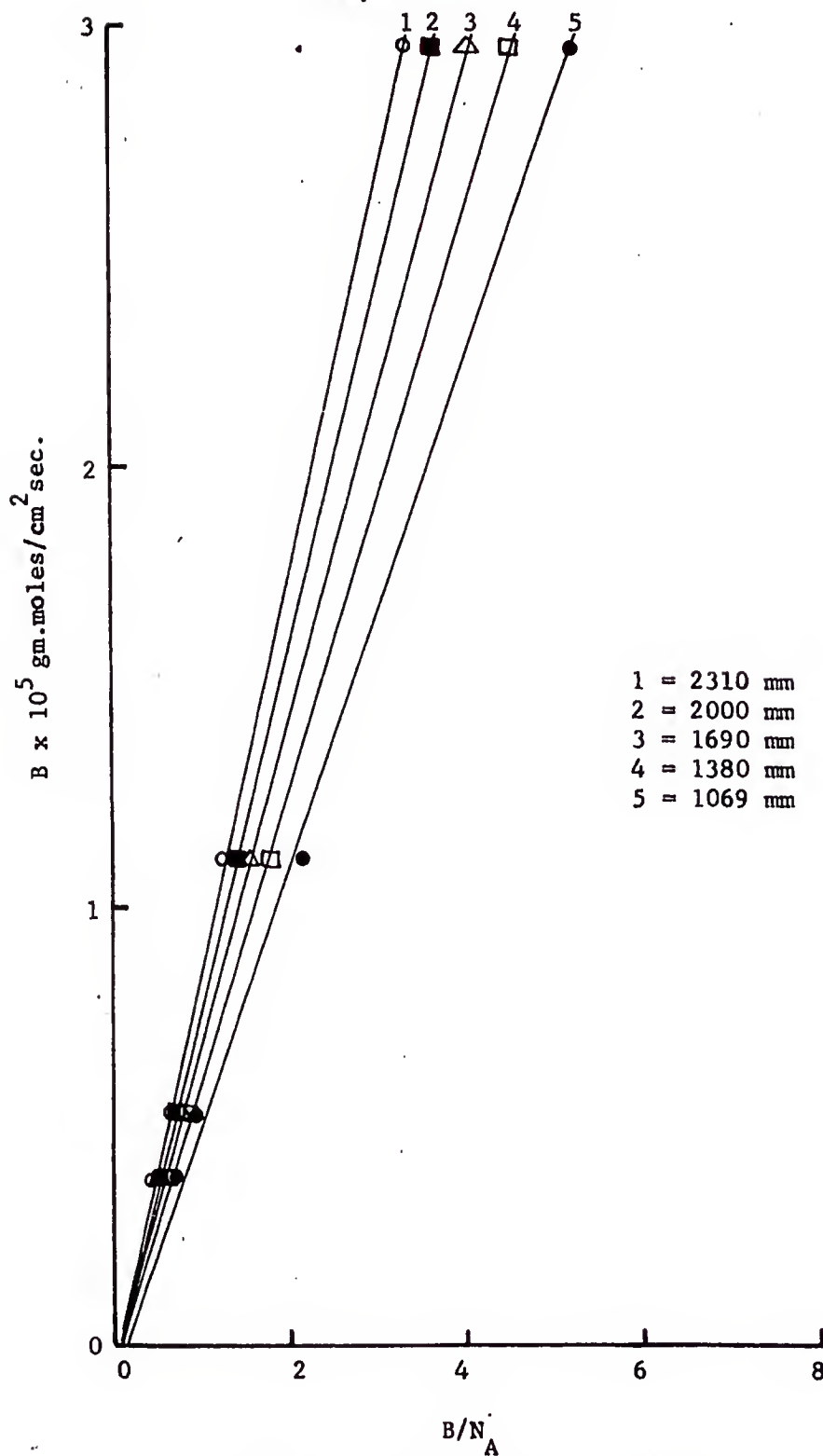


Figure 58. A Plot of B Versus B/N_A

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Temperature: 340°C

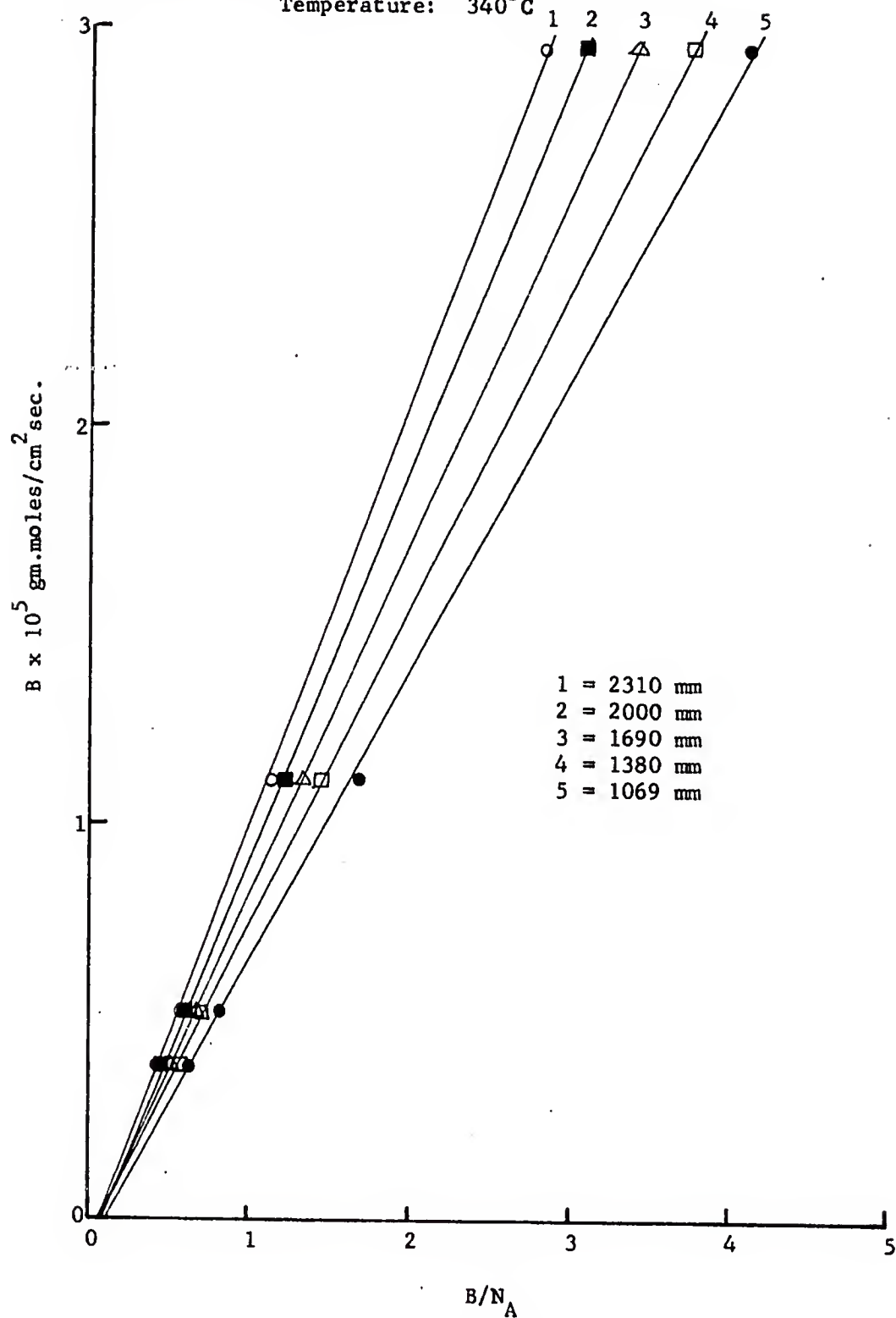


Figure 59. A Plot of B Versus B/N_A

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Temperature: 380°C

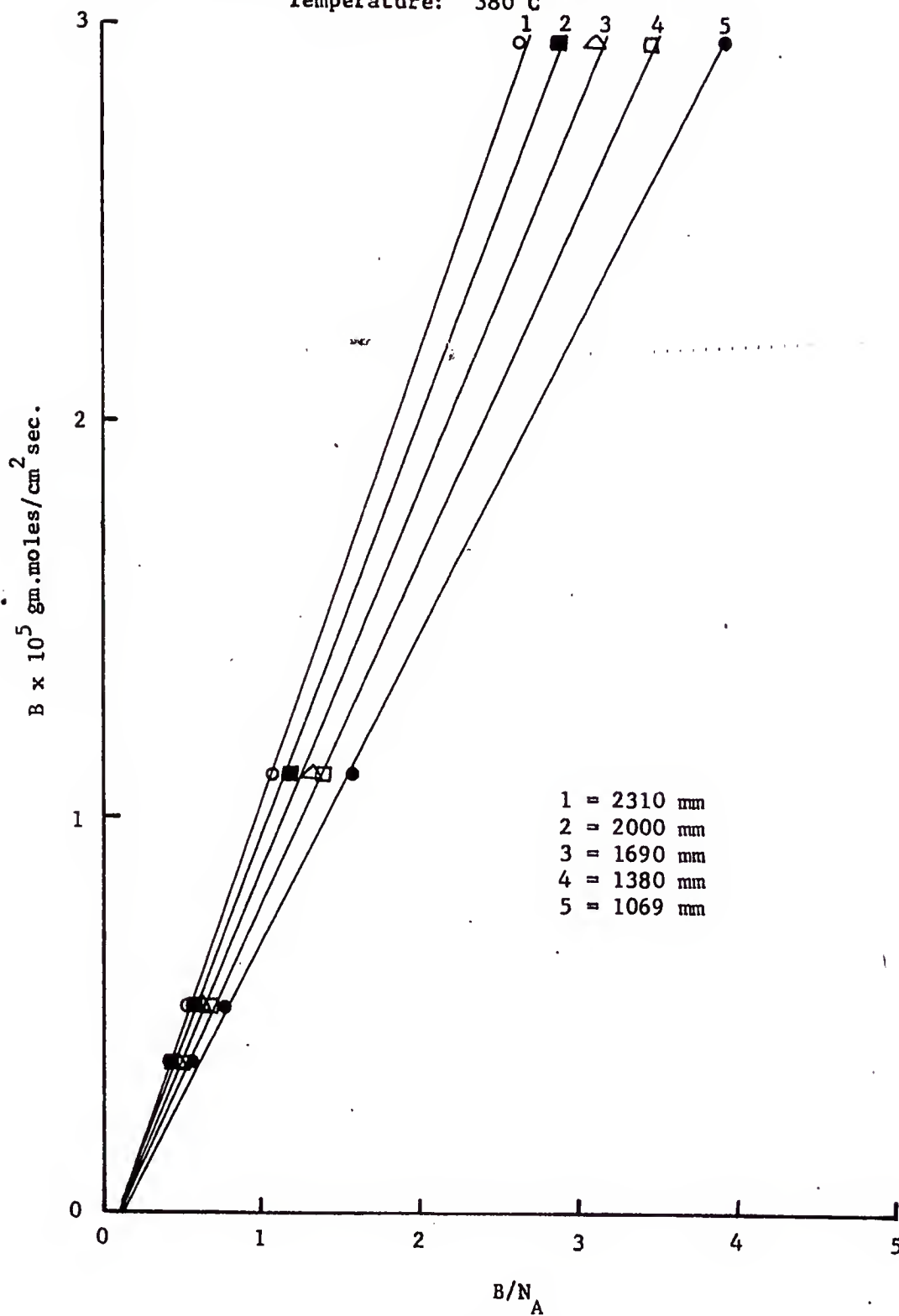
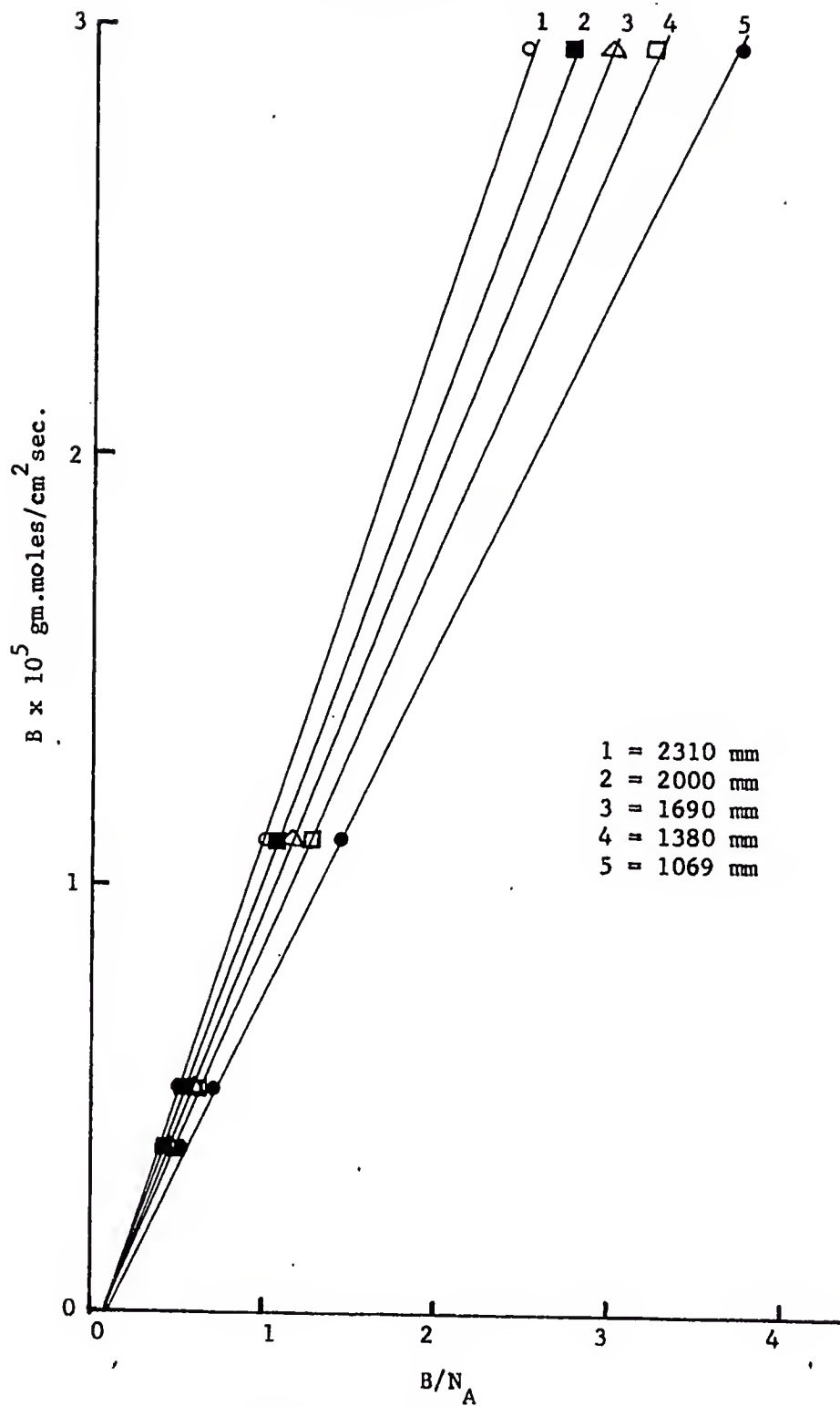


Figure 60. A Plot of B Versus B/N_A

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

Temperature: 420°C

Figure 61. A Plot of B Versus B/N_A

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂
 Temperature: 460°C

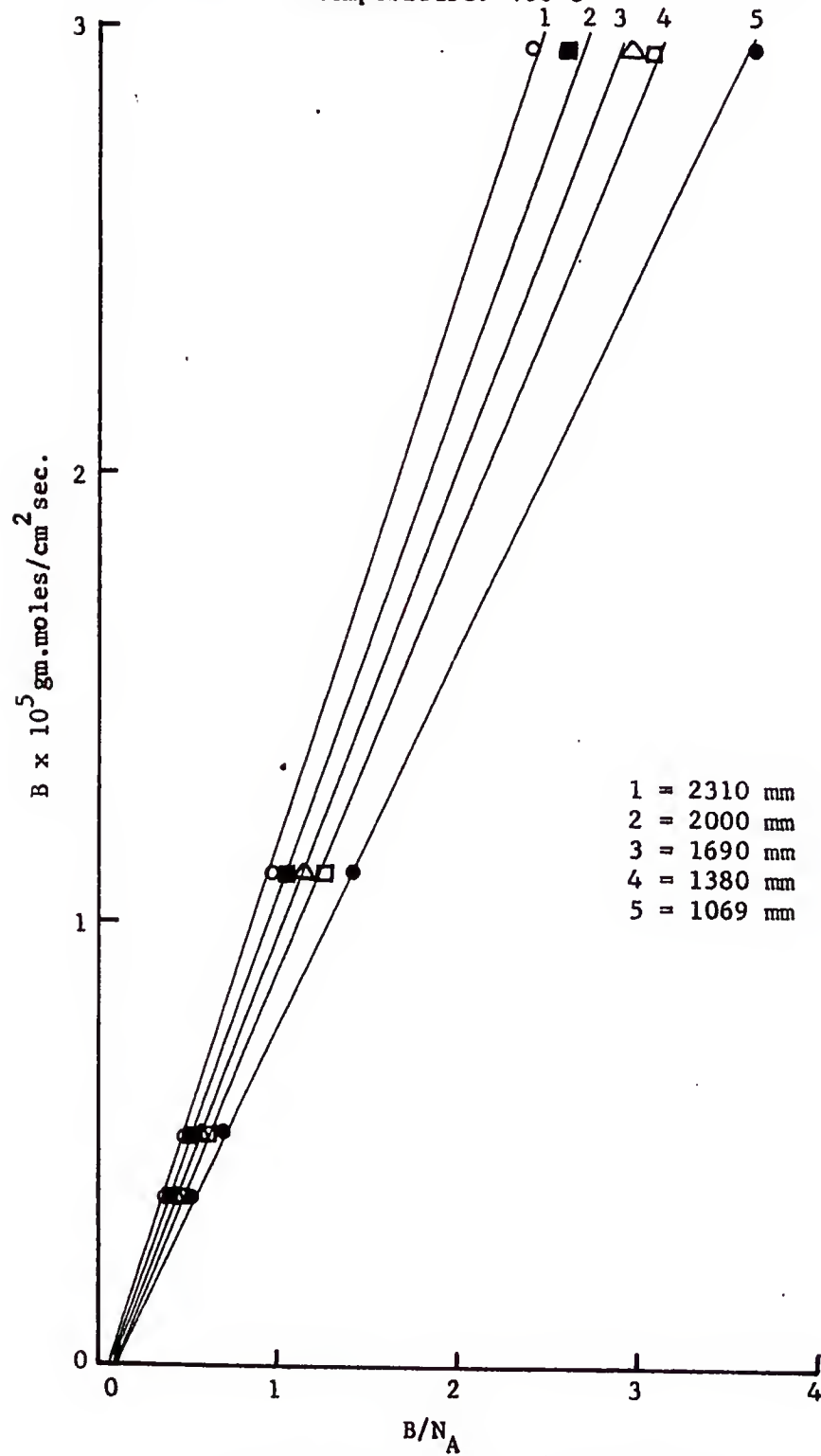


Figure 62. A Plot of B Versus B/N_A

Feed Gas Composition: 25.6% N_2 , 74.4% H_2
Temperature: 300°C

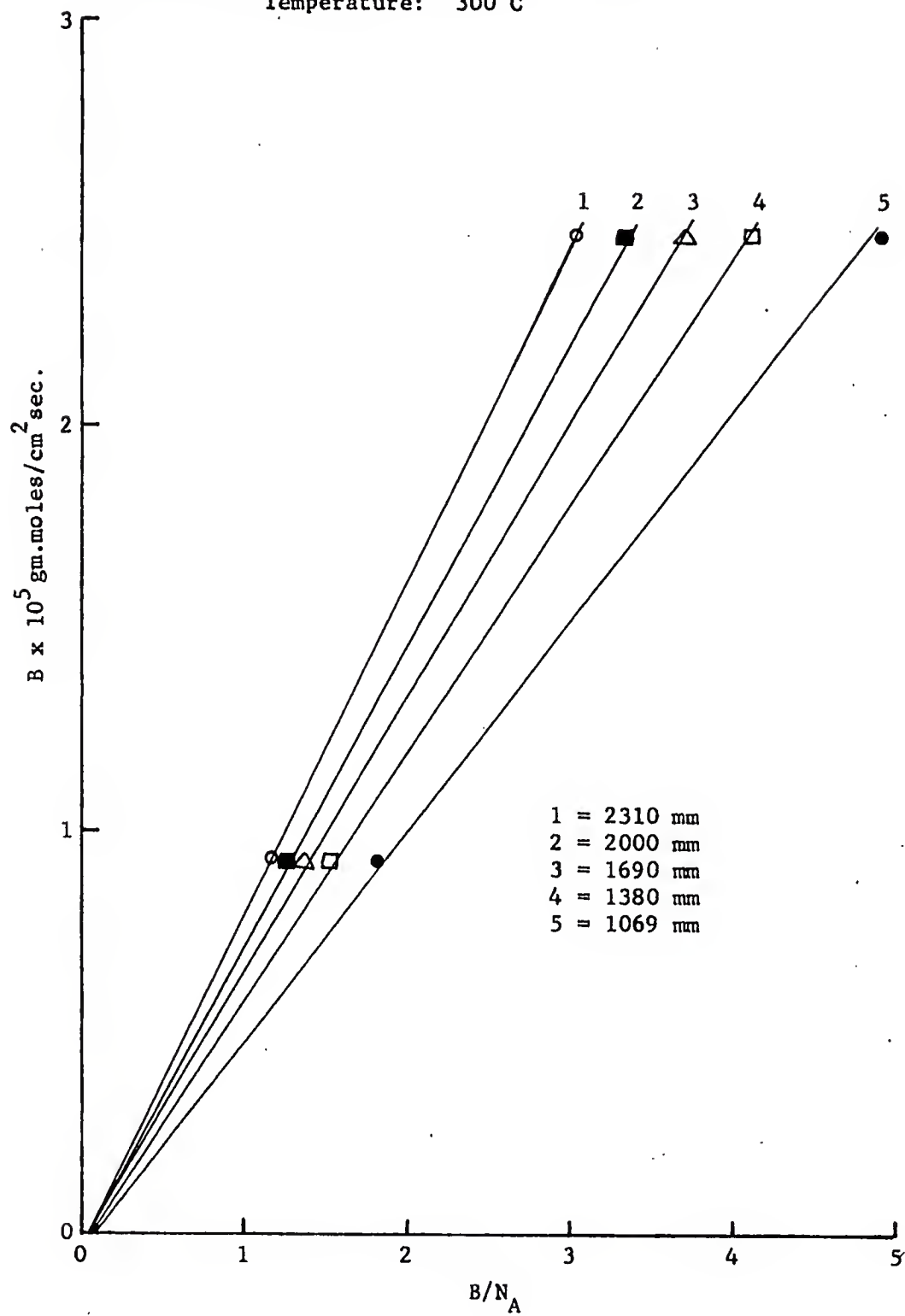
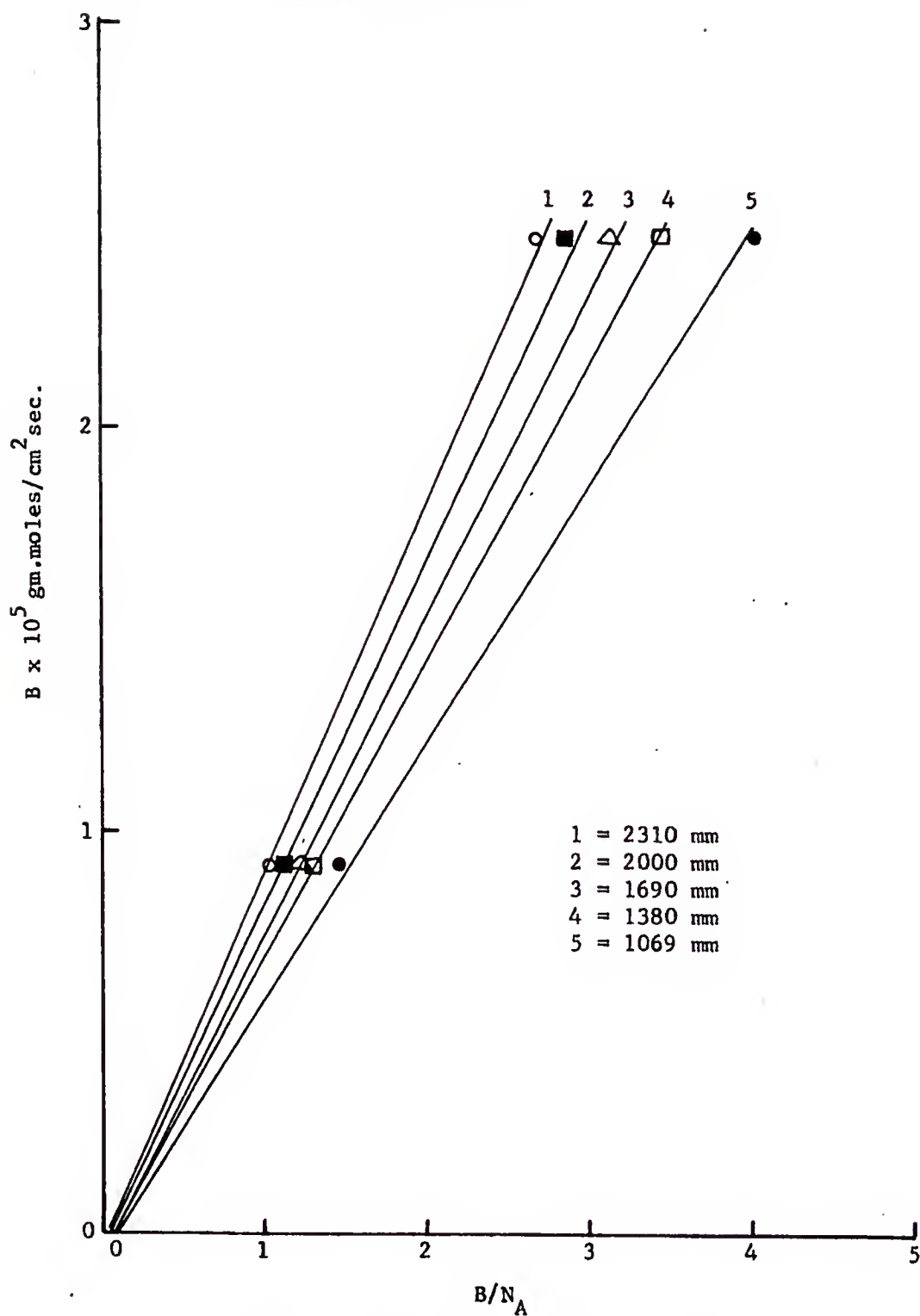


Figure 63. A Plot of B Versus B/N_A

Feed Gas Composition: 25.6% N₂, 74.4% H₂

Temperature: 340°C

Figure 64. A Plot of B Versus B/N_A

Feed Gas Composition: 25.6% N_2 , 74.4% H_2

Temperature: 380°C

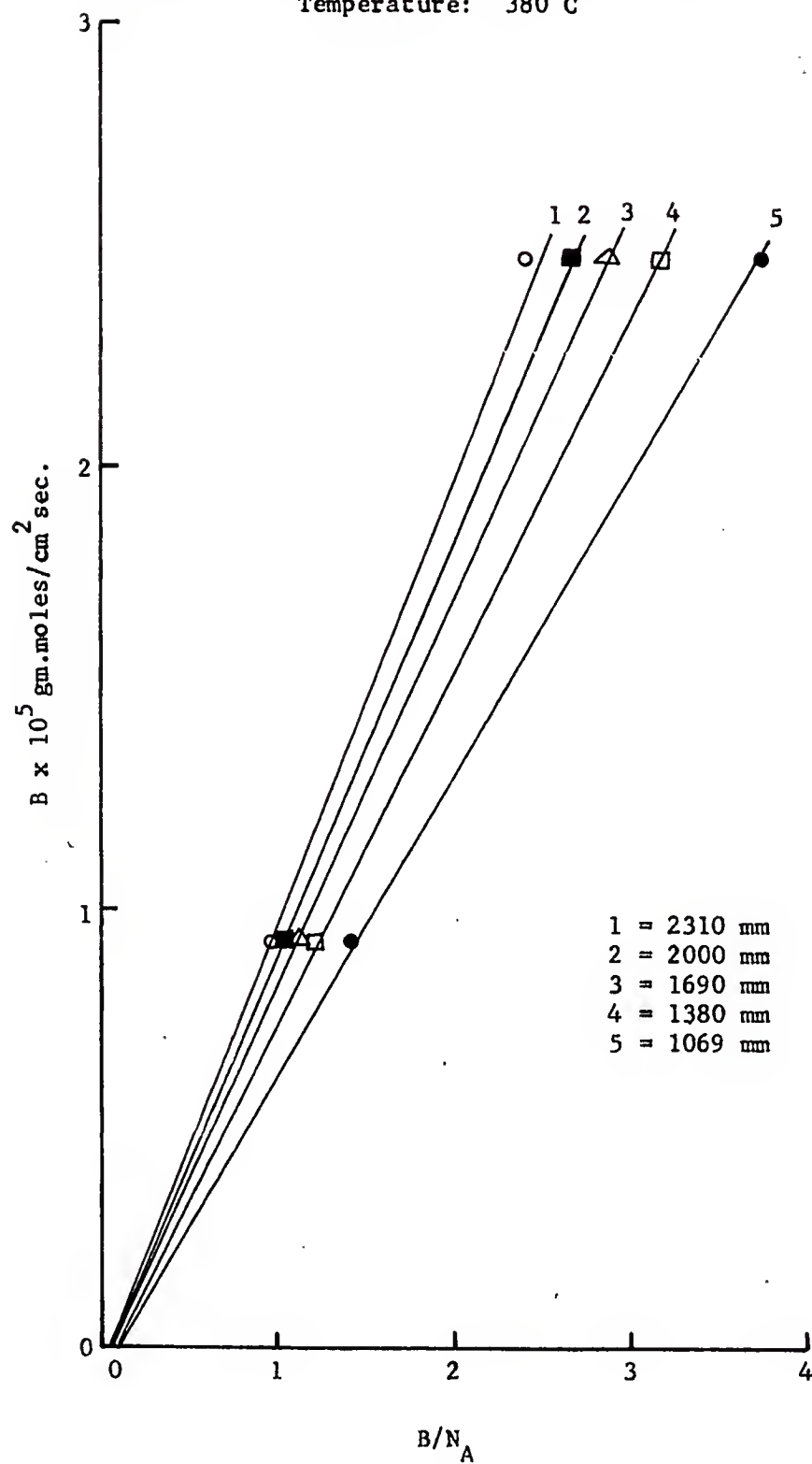


Figure 65. A Plot of B Versus B/N_A

Feed Gas Composition: 25.6% N_2 , 74.4% H_2

Temperature: 420°C

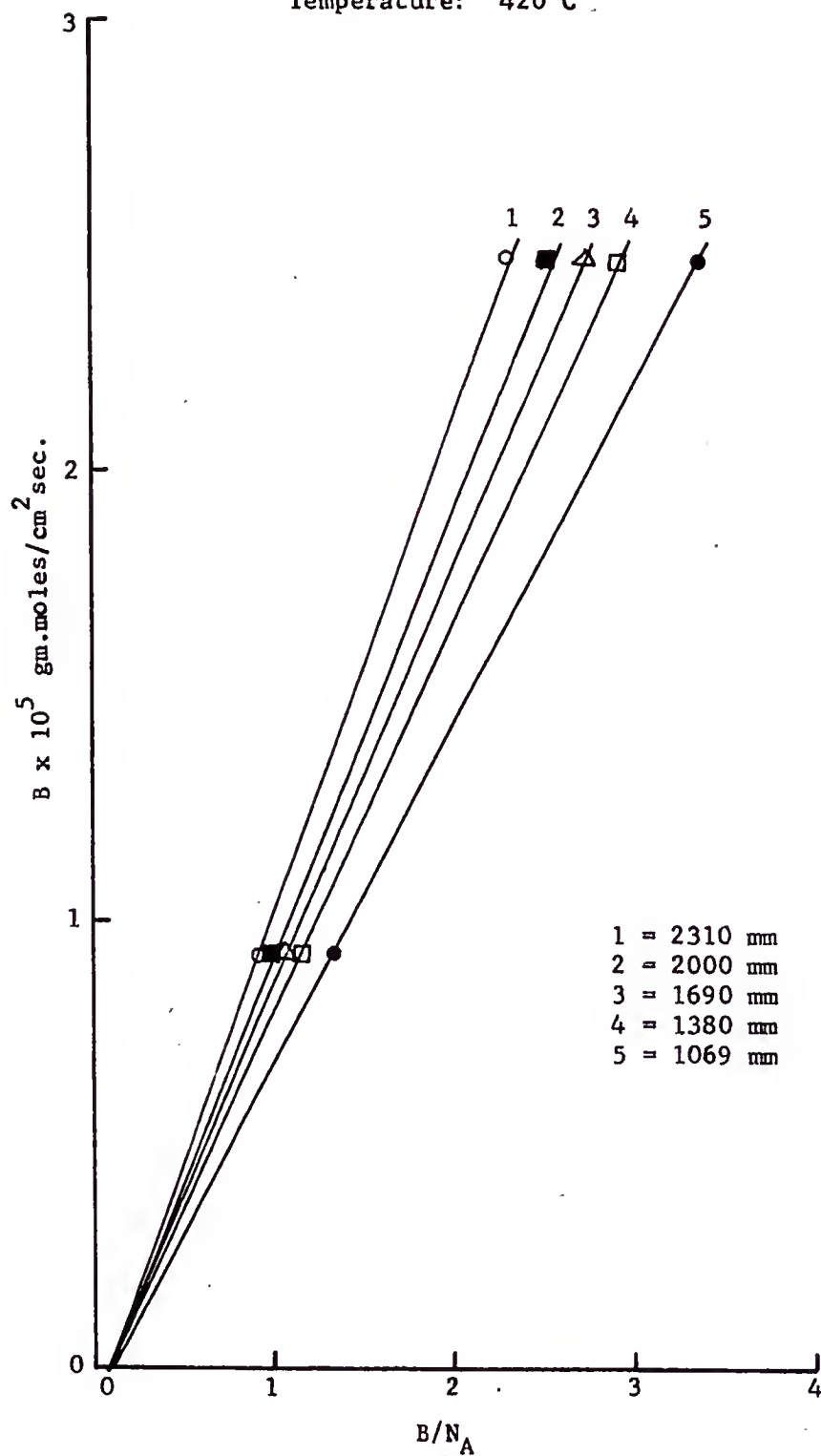


Figure 66. A Plot of B Versus B/N_A

Feed Gas Composition: 25.6% N_2 , 74.4% H_2

Temperature: $460^\circ C$

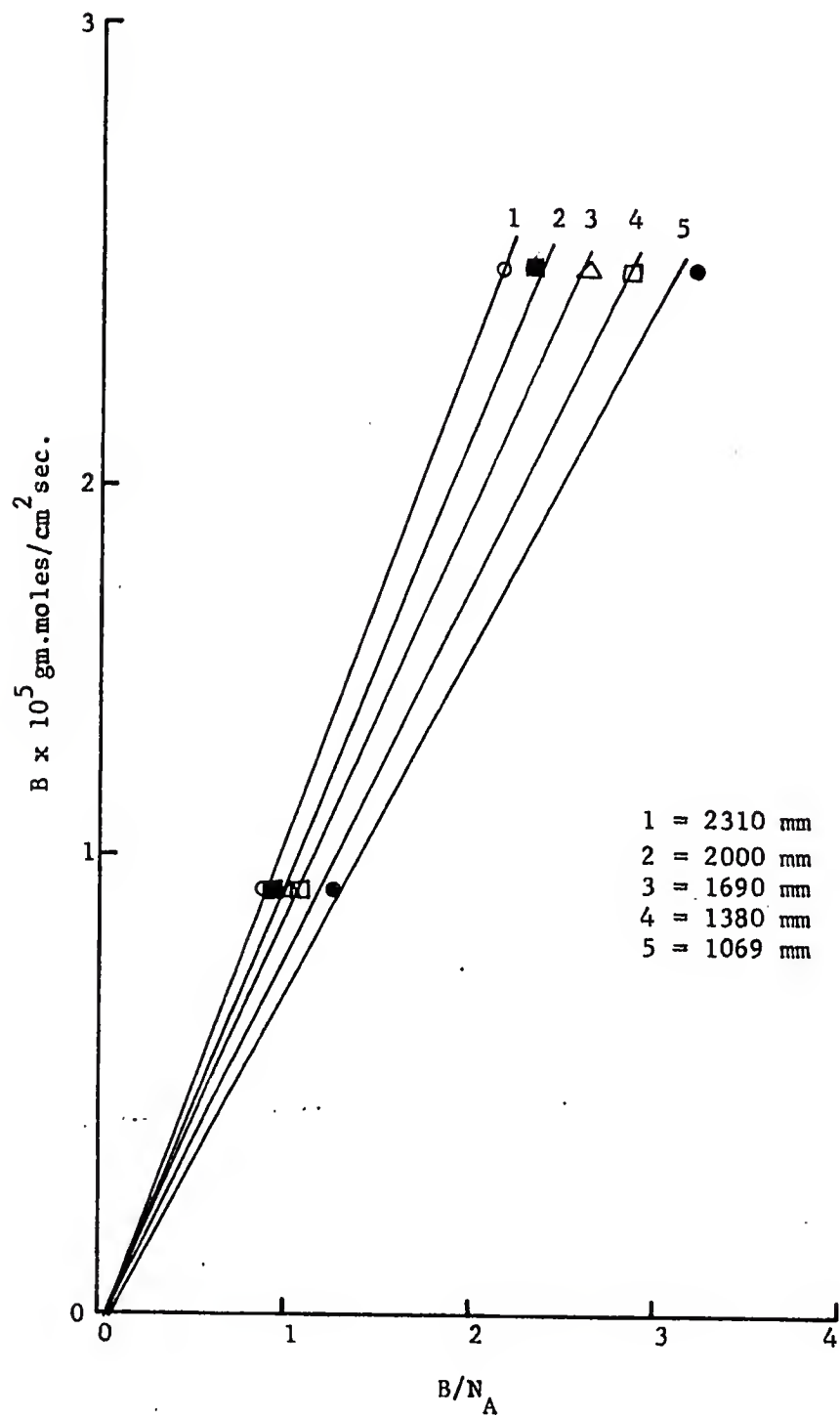


Figure 67. A Plot of B Versus B/N_A

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Temperature: 300°C

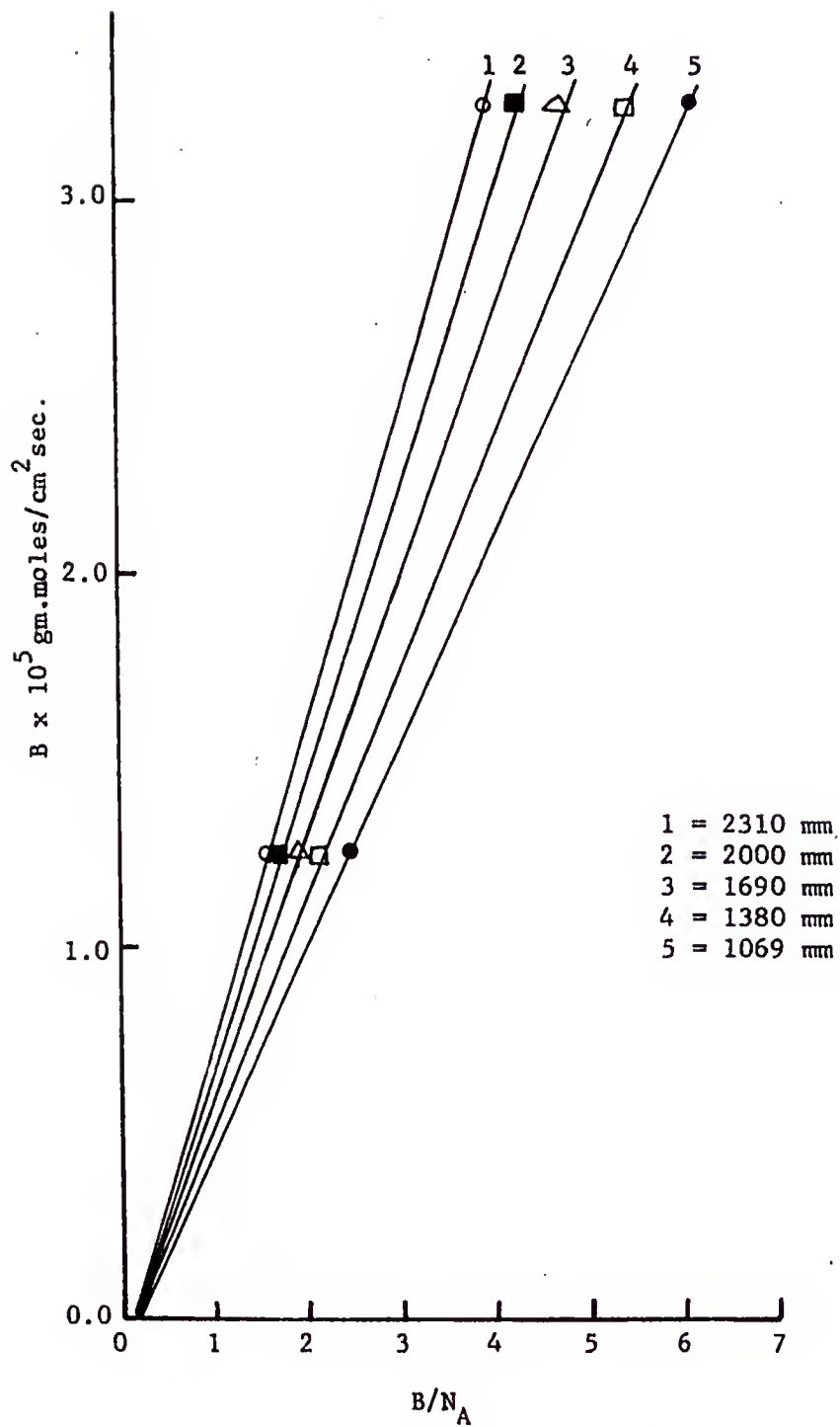


Figure 68. A Plot of B Versus B/N_A

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Temperature: 340°C

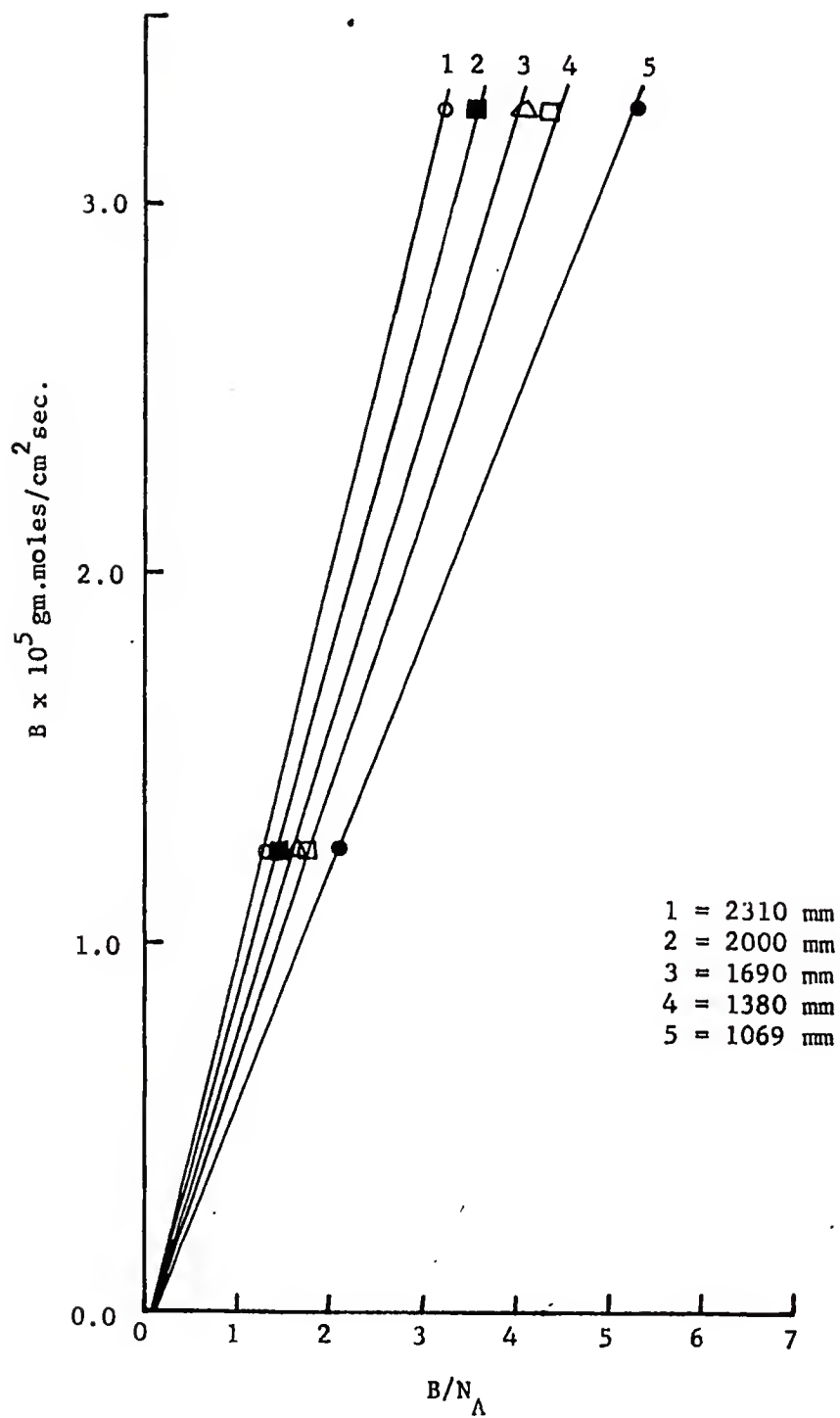


Figure 69. A Plot of B Versus B/N_A

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Temperature: 380°C

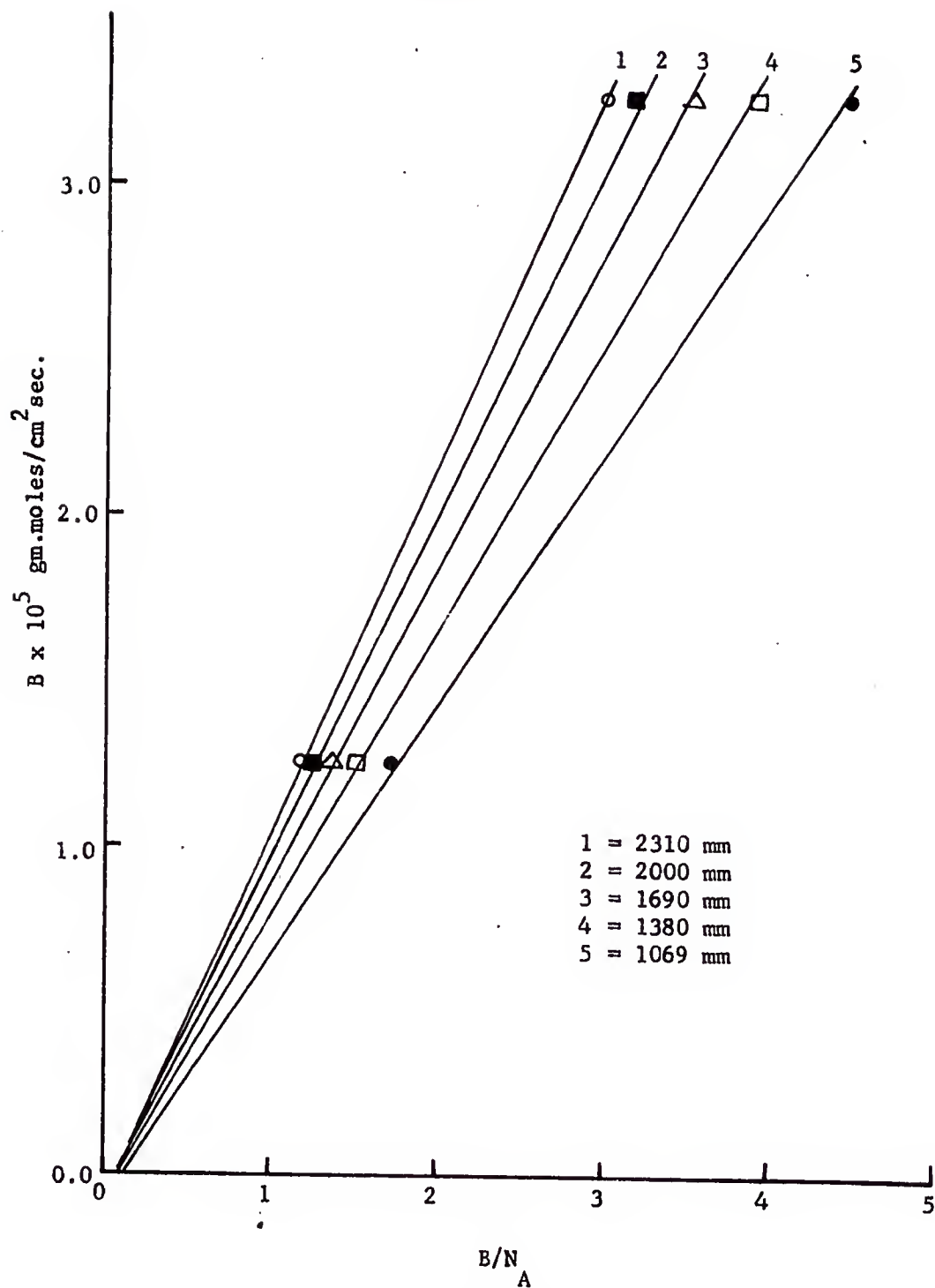


Figure 70. A Plot of B Versus B/N_A

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Temperature: 420°C

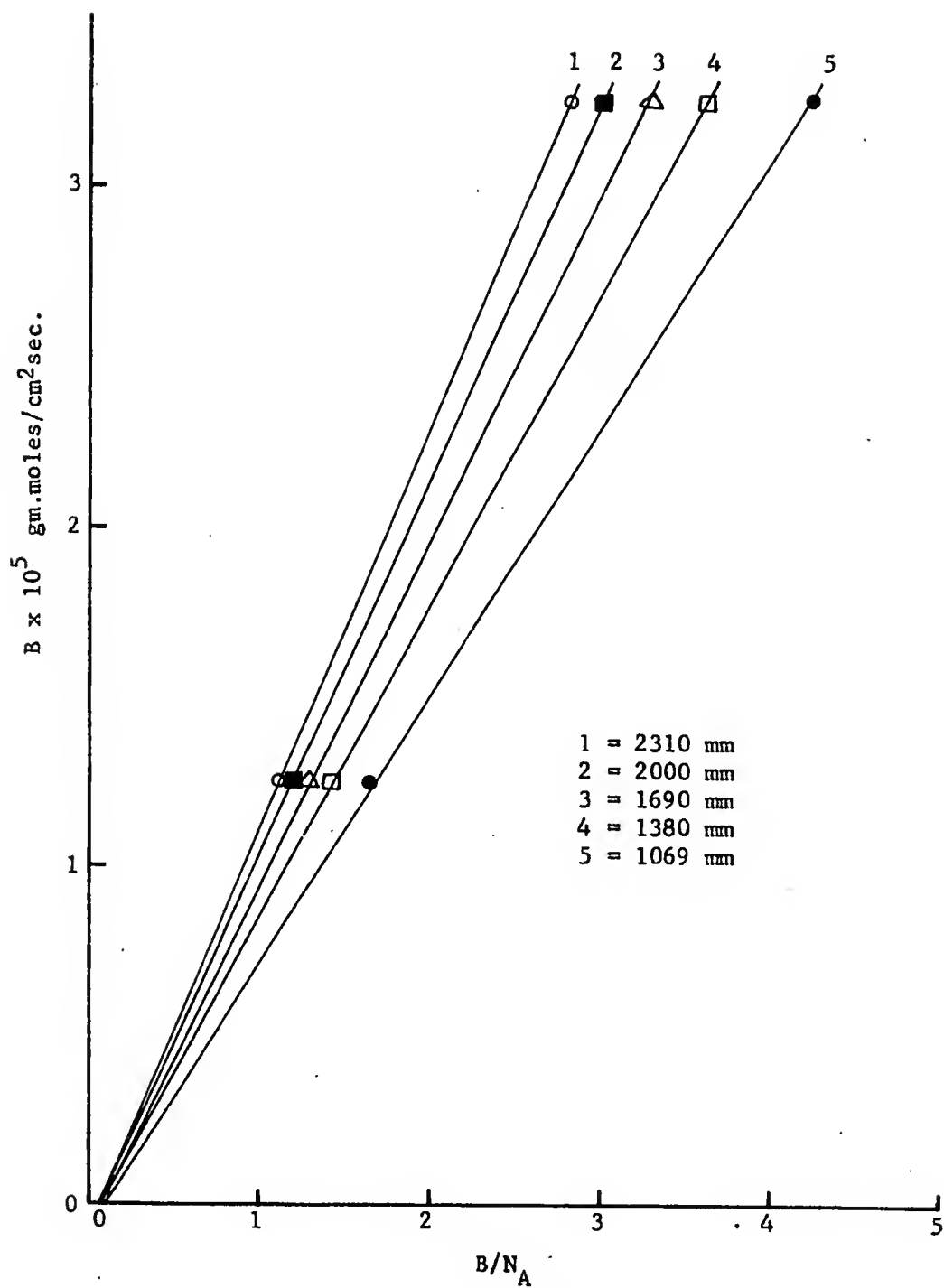


Figure 71. A Plot of B Versus B/N_A

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

Temperature: 460°C

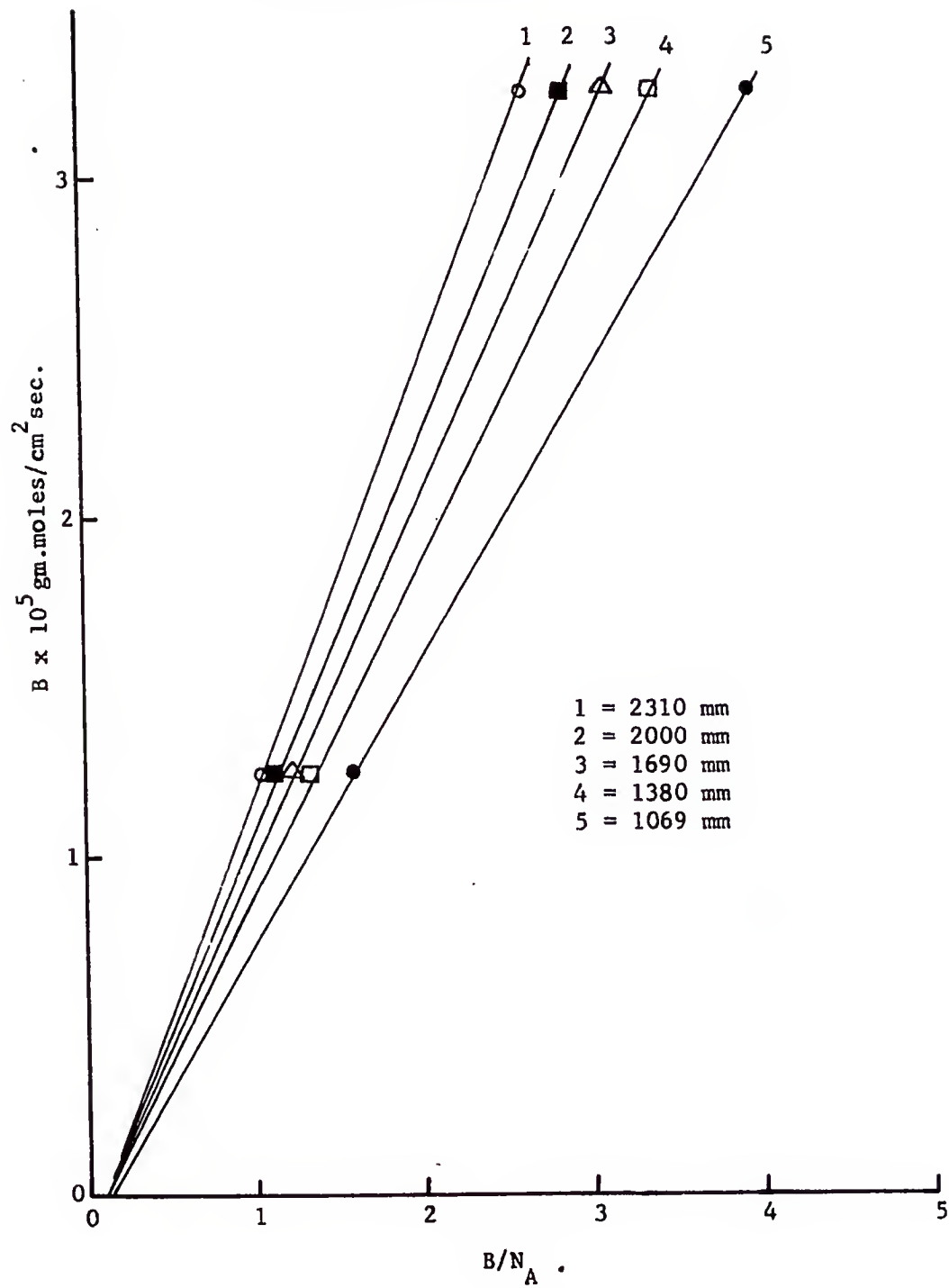


Figure 72. A Plot of B Versus B/N_A

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

Temperature: 300°C

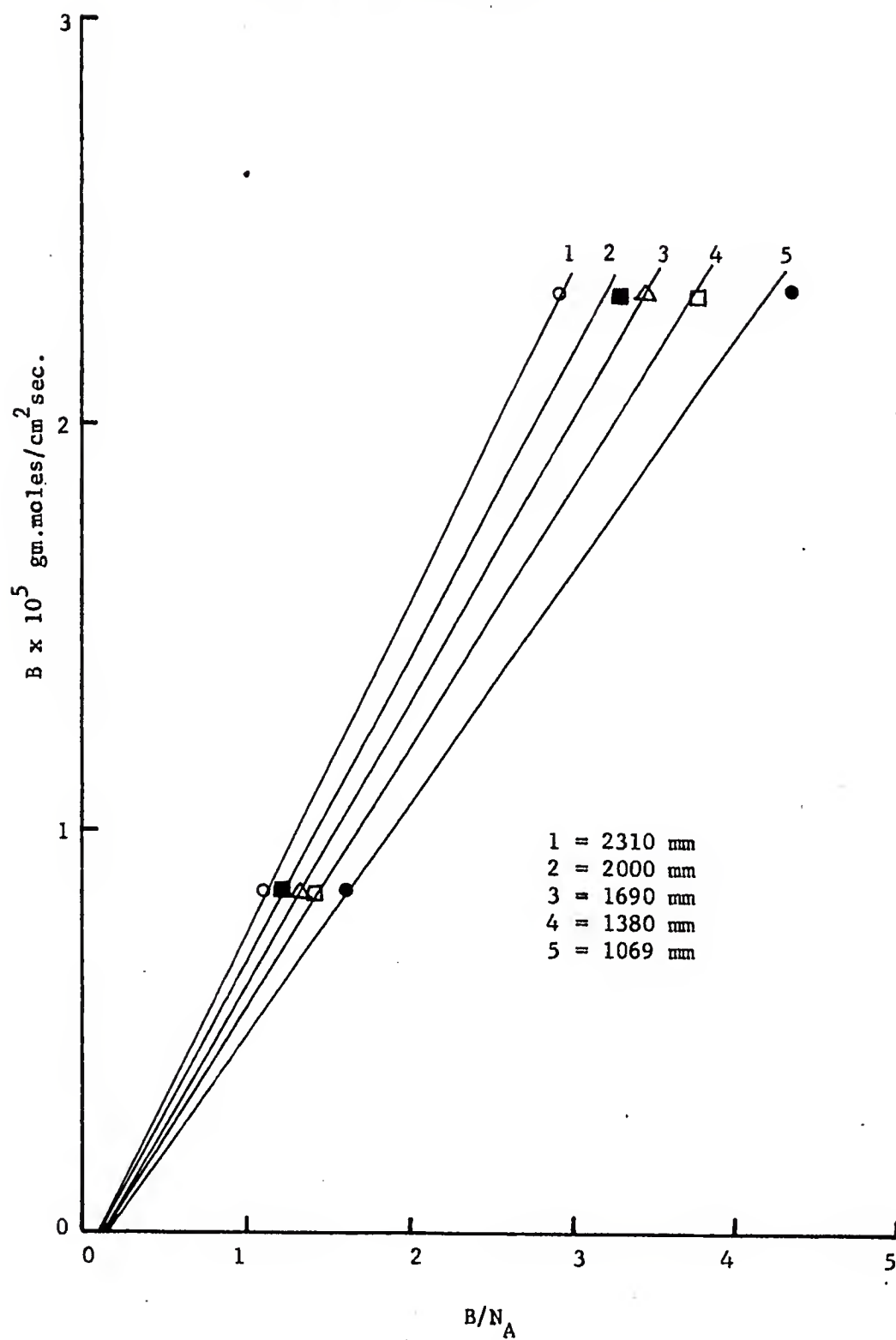


Figure 73. A Plot of B Versus B/N_A

Feed Gas Composition: 21.5% CO₂, 78.5% H₂
Temperature: 340°C

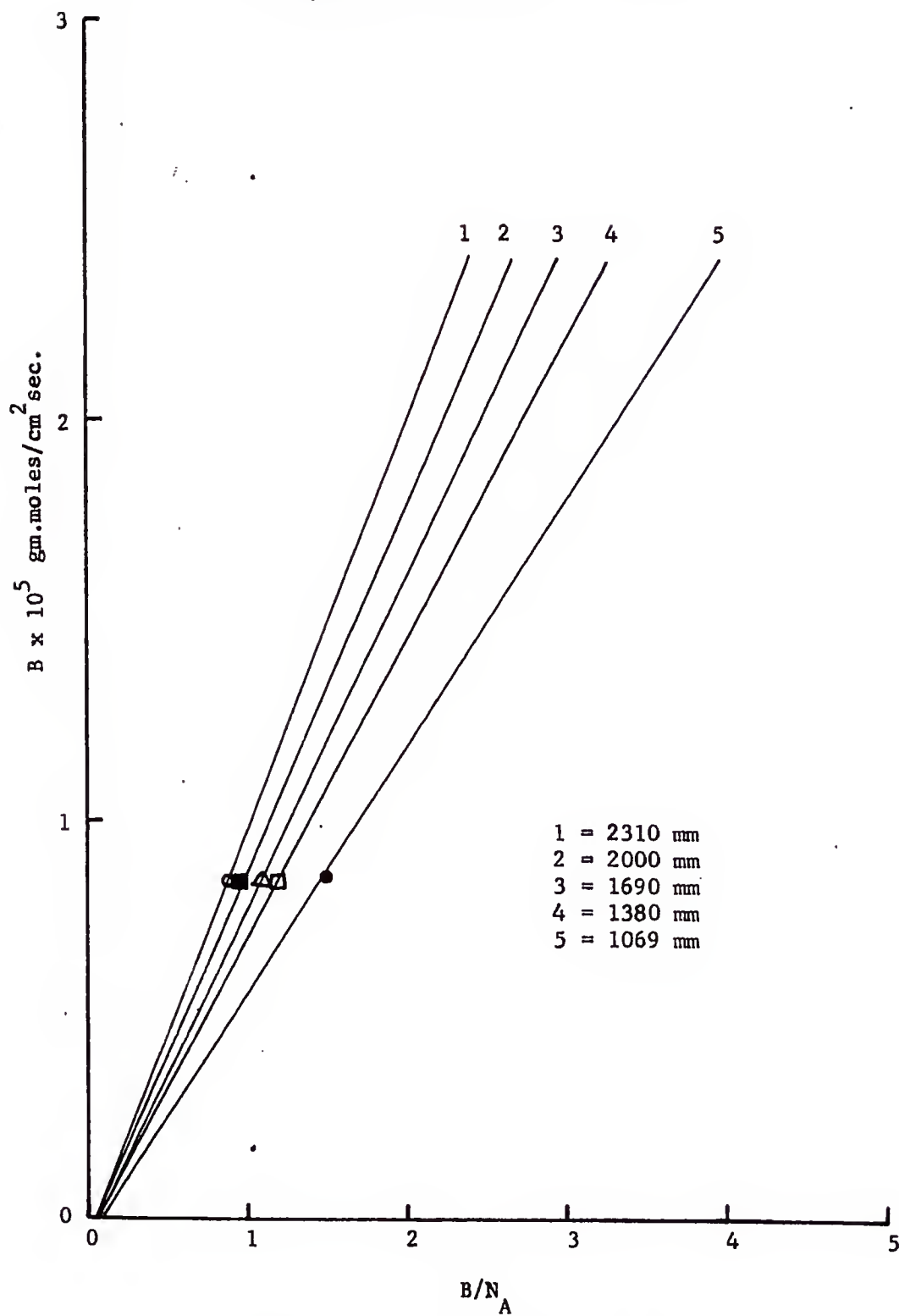
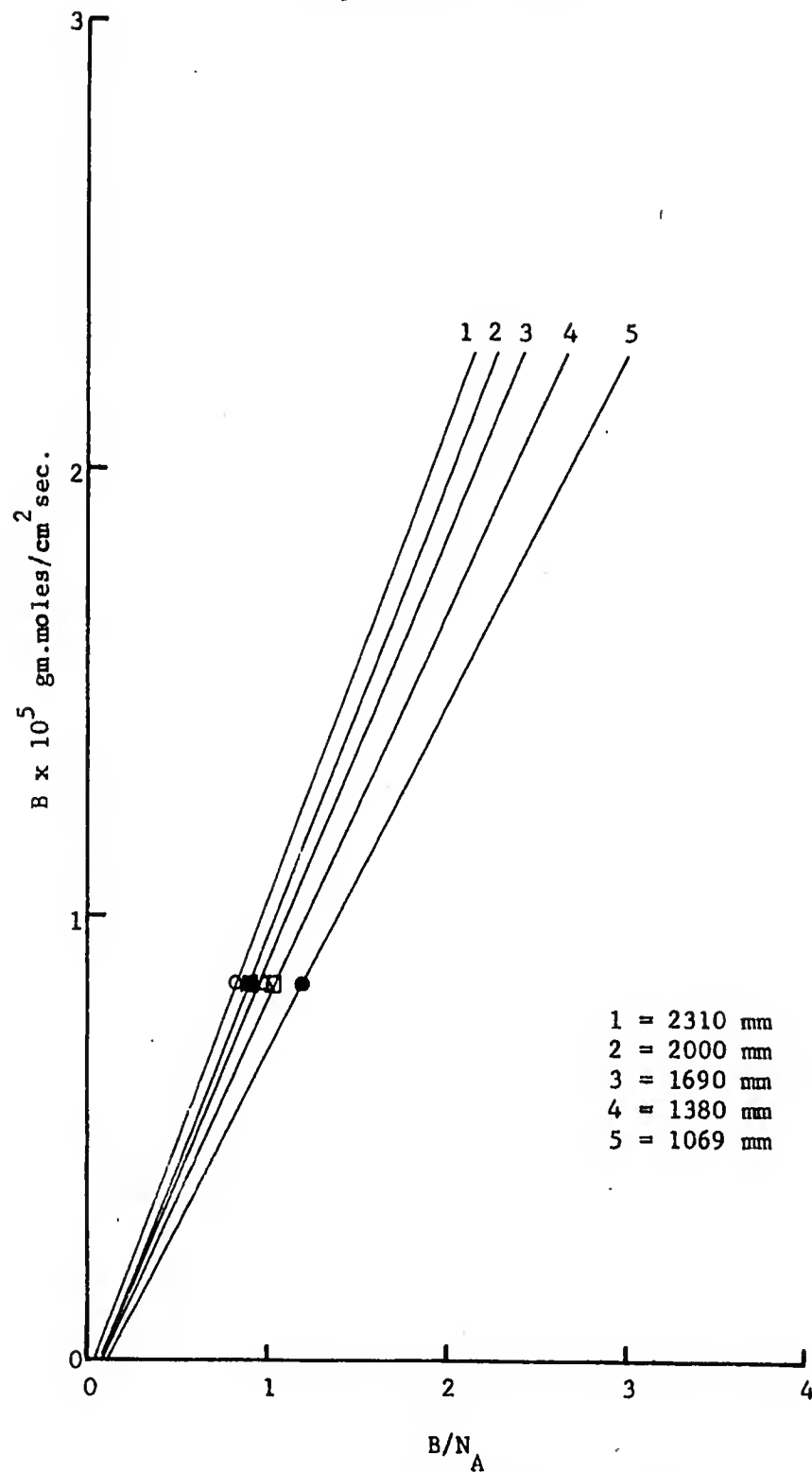


Figure 74. A Plot of B Versus B/N_A

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

Temperature: 380°C

Figure 75. A Plot of B Versus B/N_A

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

Temperature: 420°C

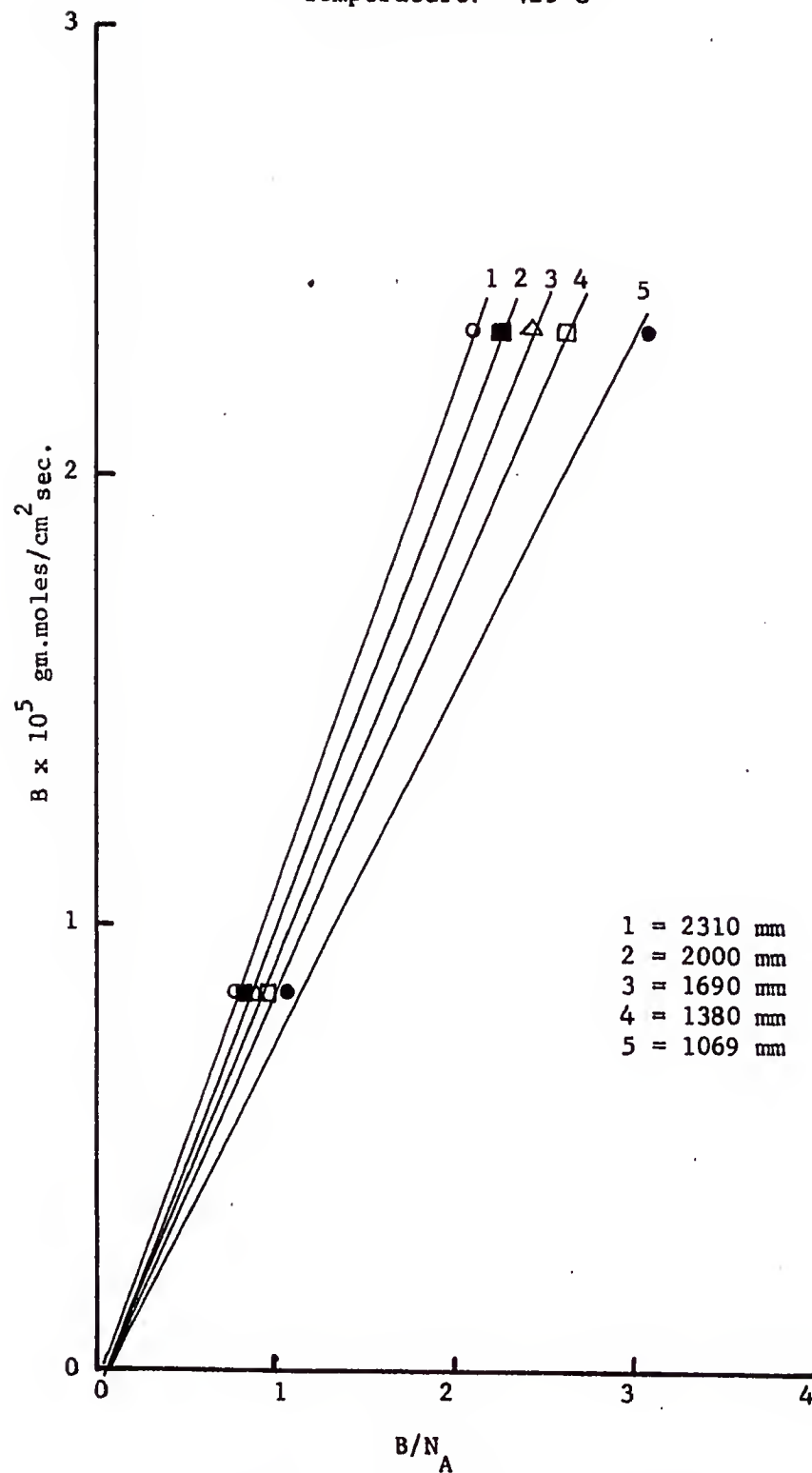
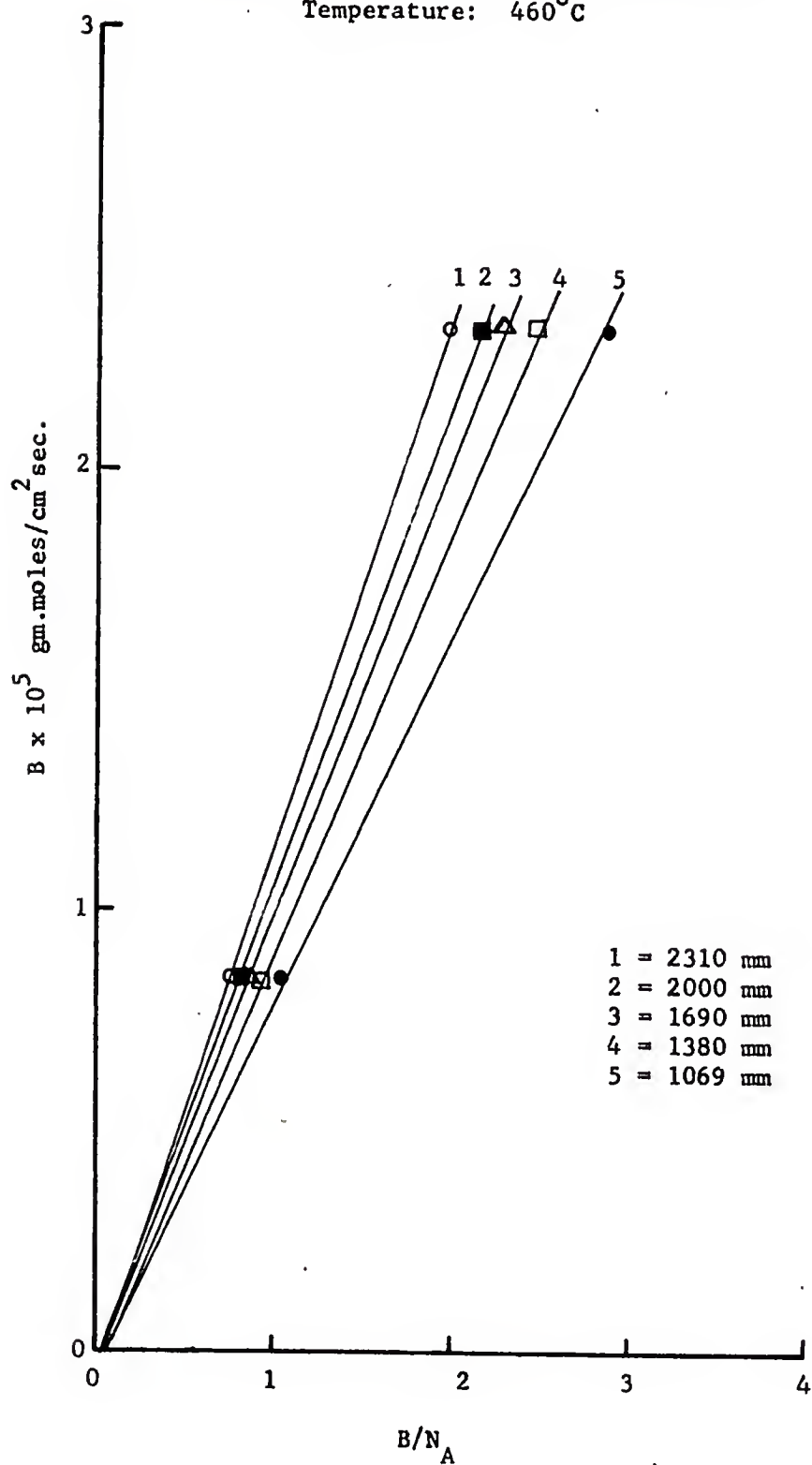


Figure 76. A Plot of B Versus B/N_A

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

Temperature: 460°C

Figure 77. A Plot of B Versus B/N_A

$$B = N_{Amax} \frac{B}{N_A} + k_2 \quad (115)$$

Equation (115) is similar to that used by DeRosset (6) for constant pressure and temperature. The significance of N_{Amax} is that it is the maximum transport rate obtainable, i.e., when the bleed rate is infinite. Values of N_{Amax} for different temperatures and pressure are tabulated in Tables 23 to 27. k_2 signifies the effectiveness of bleeding. A large k_2 means that bleeding is not very effective, while a small k_2 means that bleeding is quite effective. Values of k_2 for different temperatures are tabulated in Table 28.

Equation (115) can also be written in the form:

$$\frac{N_A}{N_{Amax}} = \frac{B}{B - k_2} \quad (116)$$

Equation (116) will be used to illustrate the significance of k_2 . At 300°C for a feed composition of 30% CH₄, 10% N₂ and 60% H₂ the value of k_2 was -3×10^{-6} . On substituting this value into Equation (116) one obtains:

$$\frac{N_A}{N_{Amax}} = \frac{B}{B + 3 \times 10^{-6}} \quad (117)$$

A plot of Equation (117) is given in Figure 78. This shows that if the value of k_2 is small, the transport rate will approach the maximum value even for a small bleed rate. To find B/N_A when N_A/N_{Amax} is around 0.8, for this particular case, Figure 78 gives $B = 1.2 \times 10^{-5}$ gm.moles/cm²sec. Then for a pressure of 1069 mm Hg, using Figure 53 gives $B/N_A \approx 3.5$. This means that to obtain 80%

TABLE 23

EFFECT OF IMPURITIES ON THE MAXIMUM RATE OF TRANSPORT
OF HYDROGEN THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

<u>Temp. °C</u>	<u>Pressure, mm Hg</u>	<u>N_{Amax} x 10⁶ gm.moles/cm²sec.</u>
300	1069	4.3
300	1380	5.0
300	1690	5.8
300	2000	6.2
300	2310	7.0
340	1069	5.3
340	1380	6.4
340	1690	7.2
340	2000	7.6
340	2310	8.1
380	1069	6.2
380	1380	6.9
380	1690	7.5
380	2000	7.9
380	2310	8.6
420	1069	6.6
420	1380	7.6
420	1690	8.2
420	2000	8.6
420	2310	9.4
460	1069	7.2
460	1380	8.5
460	1690	9.1
460	2000	9.6
460	2310	10.6

TABLE 24

EFFECT OF IMPURITIES ON THE MAXIMUM RATE OF TRANSPORT
OF HYDROGEN THROUGH PALLADIUM SILVER MEMBRANEFeed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

<u>Temp. °C</u>	<u>Pressure, mm Hg</u>	<u>N_{Amax} × 10⁶ gm.moles/cm²sec.</u>
300	1069	5.8
300	1380	6.7
300	1690	7.5
300	2000	8.2
300	2310	9.2
340	1069	7.3
340	1380	8.0
340	1690	8.9
340	2000	9.8
340	2310	10.6
380	1069	7.7
380	1380	8.7
380	1690	9.7
380	2000	10.5
380	2310	11.4
420	1069	8.2
420	1380	9.3
420	1690	10.2
420	2000	10.9
420	2310	12.0
460	1069	8.4
460	1380	9.8
460	1690	10.4
460	2000	11.0
460	2310	12.5

TABLE 25

EFFECT OF IMPURITIES ON THE MAXIMUM RATE OF TRANSPORT
OF HYDROGEN THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 25.6% N₂, 74.4% H₂

<u>Temp. °C</u>	<u>Pressure, mm Hg</u>	<u>N_{Amax} x 10⁶ gm.moles/cm² sec.</u>
300	1069	5.4
300	1380	6.2
300	1690	6.9
300	2000	7.5
300	2310	8.6
340	1069	6.4
340	1380	7.4
340	1690	7.9
340	2000	8.4
340	2310	9.0
380	1069	6.7
380	1380	8.0
380	1690	8.7
380	2000	9.4
380	2310	10.1
420	1069	7.6
420	1380	8.7
420	1690	9.3
420	2000	10.0
420	2310	10.9
460	1069	8.5
460	1380	9.1
460	1690	10.0
460	2000	10.9
460	2310	11.7

TABLE 26

EFFECT OF IMPURITIES ON THE MAXIMUM RATE OF TRANSPORT
OF HYDROGEN THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

<u>Temp. °C</u>	<u>Pressure, mm Hg</u>	<u>N_{Amax} × 10⁶ gm.moles/cm²sec.</u>
300	1069	5.5
300	1380	6.1
300	1690	6.9
300	2000	7.7
300	2310	8.5
340	1069	6.4
340	1380	7.5
340	1690	8.1
340	2000	8.9
340	2310	10.0
380	1069	7.5
380	1380	8.6
380	1690	9.4
380	2000	10.2
380	2310	10.9
420	1069	8.5
420	1380	9.0
420	1690	10.1
420	2000	11.0
420	2310	12.0
460	1069	8.4
460	1380	9.7
460	1690	10.7
460	2000	11.6
460	2310	12.7

TABLE 27

EFFECT OF IMPURITIES ON THE MAXIMUM RATE OF TRANSPORT
OF HYDROGEN THROUGH PALLADIUM SILVER MEMBRANE

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

<u>Temp. °C</u>	<u>Pressure, mm Hg</u>	<u>N_{Amax} x 10⁶ gm.moles/cm² sec.</u>
300	1069	5.8
300	1380	6.5
300	1690	7.0
300	2000	7.5
300	2310	8.1
340	1069	6.2
340	1380	7.5
340	1690	8.4
340	2000	9.2
340	2310	10.3
380	1069	7.5
380	1380	8.8
380	1690	9.6
380	2000	10.2
380	2310	10.7
420	1069	8.0
420	1380	9.1
420	1690	9.7
420	2000	10.5
420	2310	11.3
460	1069	8.4
460	1380	9.6
460	1690	10.4
460	2000	11.0
460	2310	12.0

TABLE 28
 TABULATION OF k_2 IN EQUATION (115)
 FOR DIFFERENT GASES AND TEMPERATURE

<u>Feed Gas Composition</u>	<u>Temperature °C</u>	<u>$-(k_2 \times 10^6)$</u>
30% CH ₄ , 10% N ₂ , 60% H ₂	300	3.0
	340	1.4
	380	0.8
	420	1.0
	460	2.0
10% CH ₄ , 10% N ₂ , 80% H ₂	300	0.8
	340	0.8
	380	1.0
	420	0.8
	460	0.8
25.6% N ₂ , 74.4% H ₂	300	0.4
	340	0.5
	380	0.6
	420	0.8
	460	0.6
19.8% CH ₄ , 80.2% H ₂	300	1.0
	340	0.8
	380	0.8
	420	0.8
	460	1.0
21.5% CO ₂ , 78.5% H ₂	300	0.8
	340	0.6
	380	0.6
	420	0.4
	460	0.4

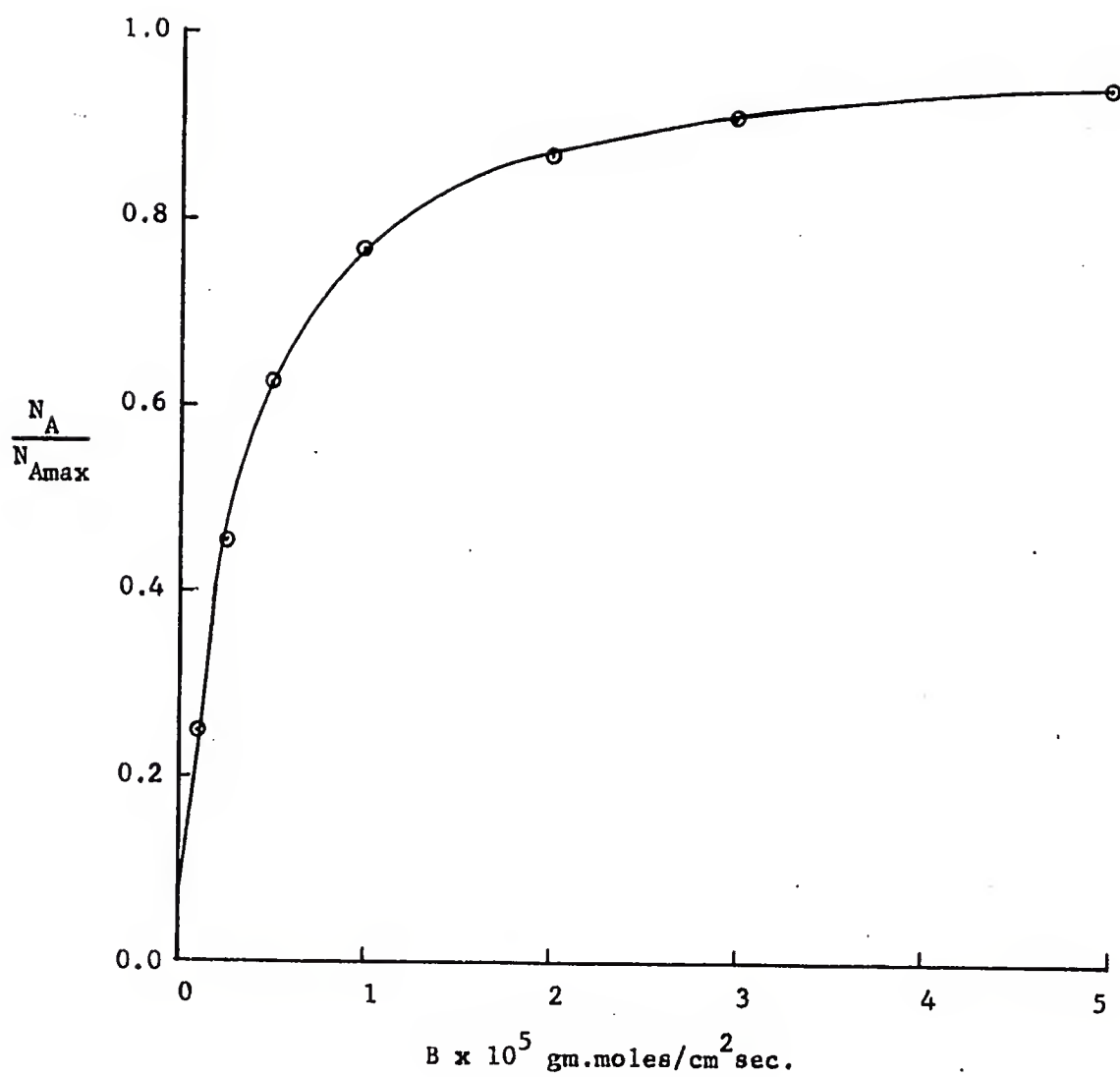


Figure 78. A Plot of $\frac{N_A}{(N_A)_{MAX}}$ Versus B

efficiency by bleeding, the bleed rate must be 3.5 times larger than the transport rate, i.e., almost 78% of the feed must be discharged in the bleed.

The theoretical verification of Equation (116) can be traced to Equation (97):

$$N_A = \frac{DC_1}{L} \left(\frac{k_G}{k_G + \frac{1}{L}} \right) \quad (118)$$

if

$$\frac{DC_1}{L} = N_{Amax} \quad (119)$$

than

$$\frac{B}{B - k_2} = \frac{k_G}{k_G + \frac{1}{L}} \quad (120)$$

From Equation (120) therefore

$$k_G = k_4 B \quad (121)$$

In other words k_G is directly proportional to the bleed rate. The significance of k_G is that it is a hypothetical mass transfer coefficient in the gas phase, where the concentrations in the gas phase are expressed in terms of the concentration of the solid.

If Equation (119) is true, this means that the effect of impurities is purely in the form of gas film resistance. This was not found to be true. When the values of N_{Amax} are fitted to Equation (108), the usual N_{Amax} , T, P plot of which are shown in Figures 79 to 88, one gets the fitted constant tabulated in Table 29. The energy of activation was higher when impurities were introduced, which indicates that there is a surface effect such as adsorption which is causing this deviation.

Feed Gas Composition: 30% CH₄, 10% N₂, 60% H₂

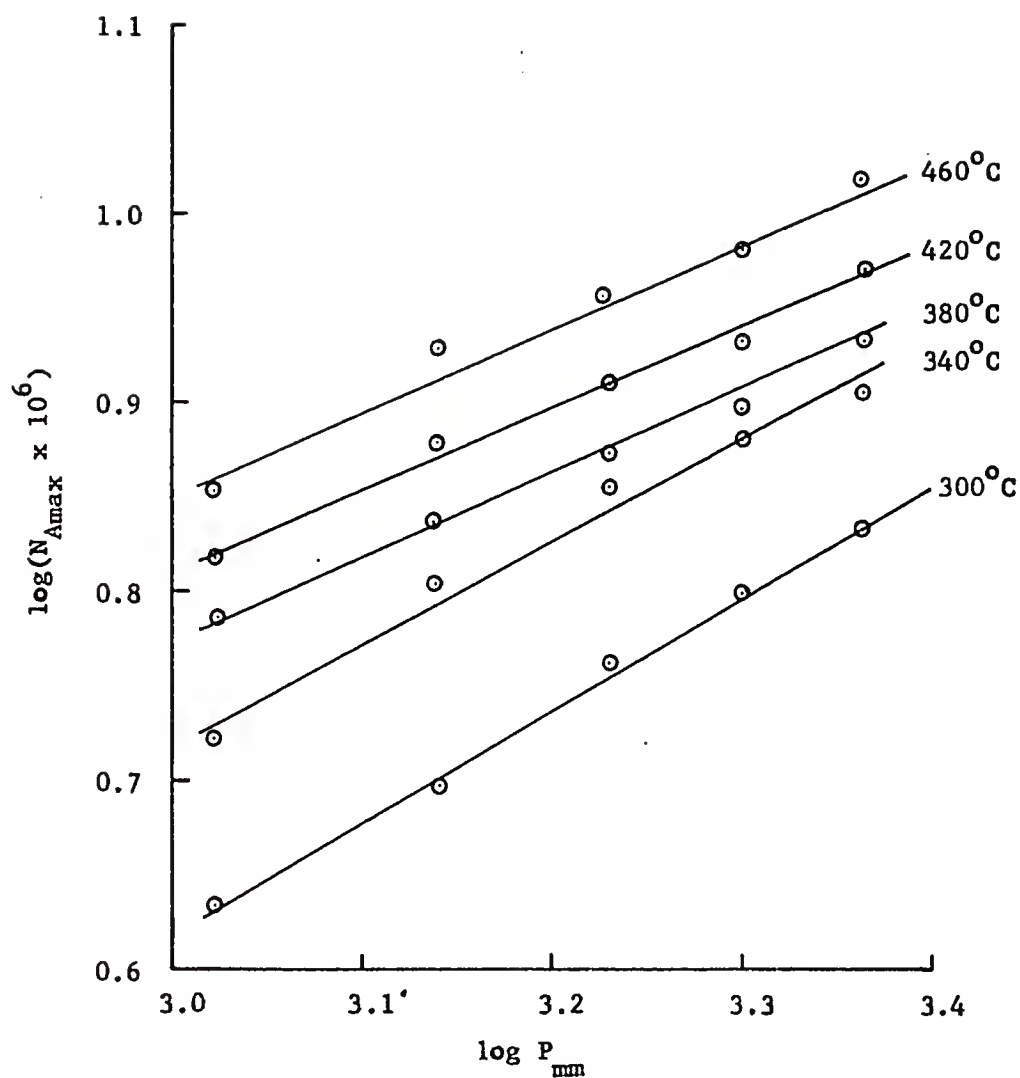


Figure 79. Effect of Impurities on the Maximum Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

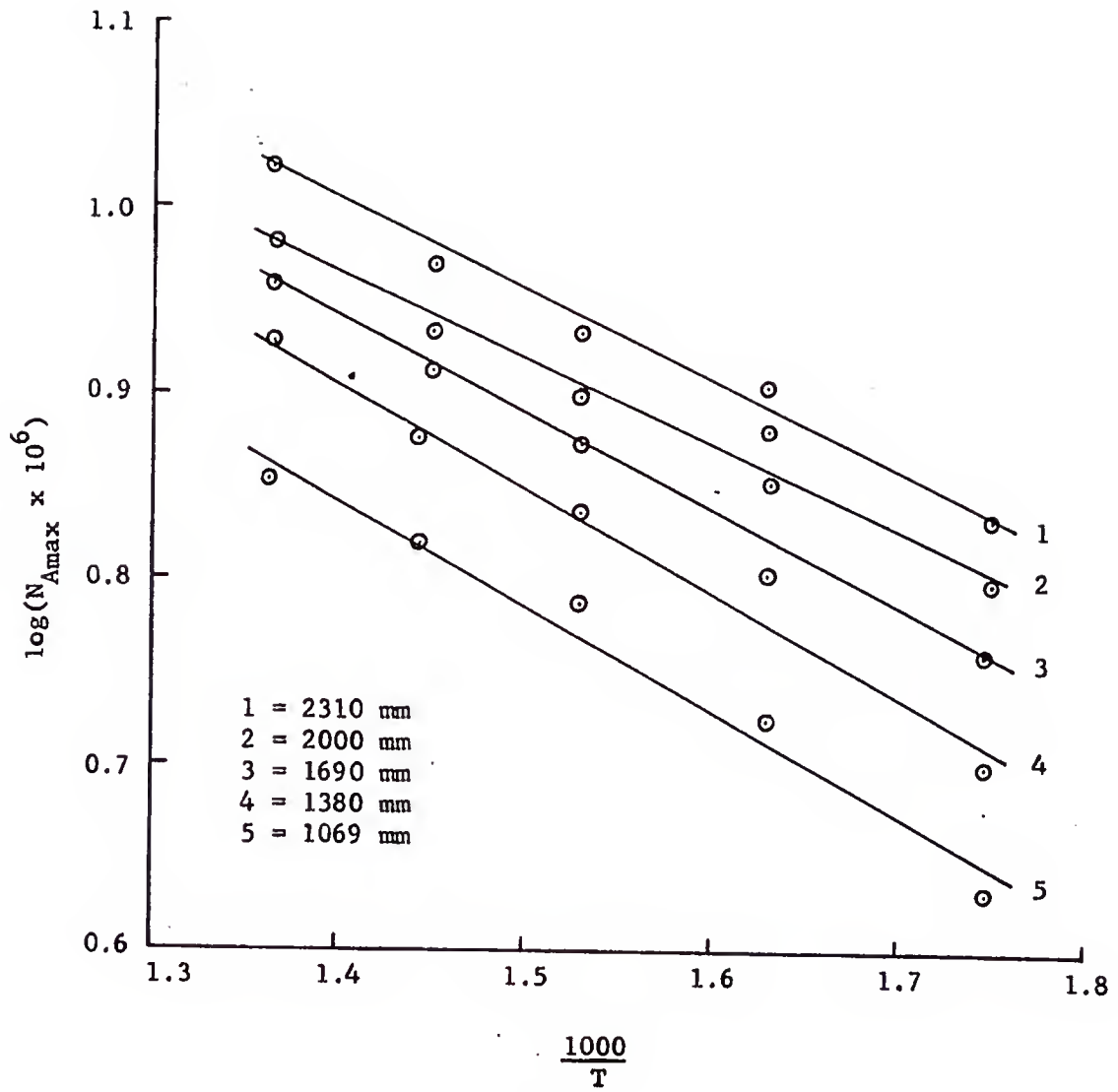


Figure 80. Determination of the Energy of Activation

Feed Gas Composition: 10% CH₄, 10% N₂, 80% H₂

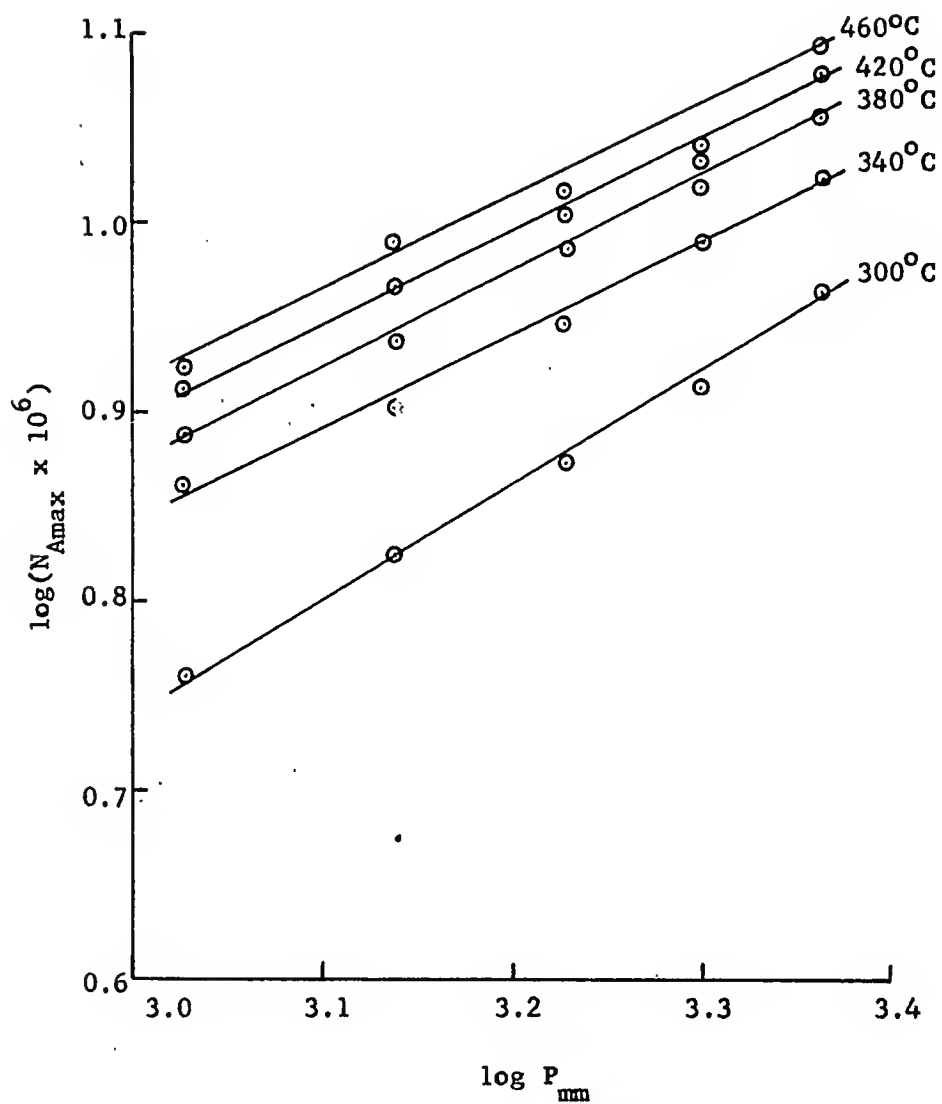


Figure 81. Effect of Impurities on the Maximum Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

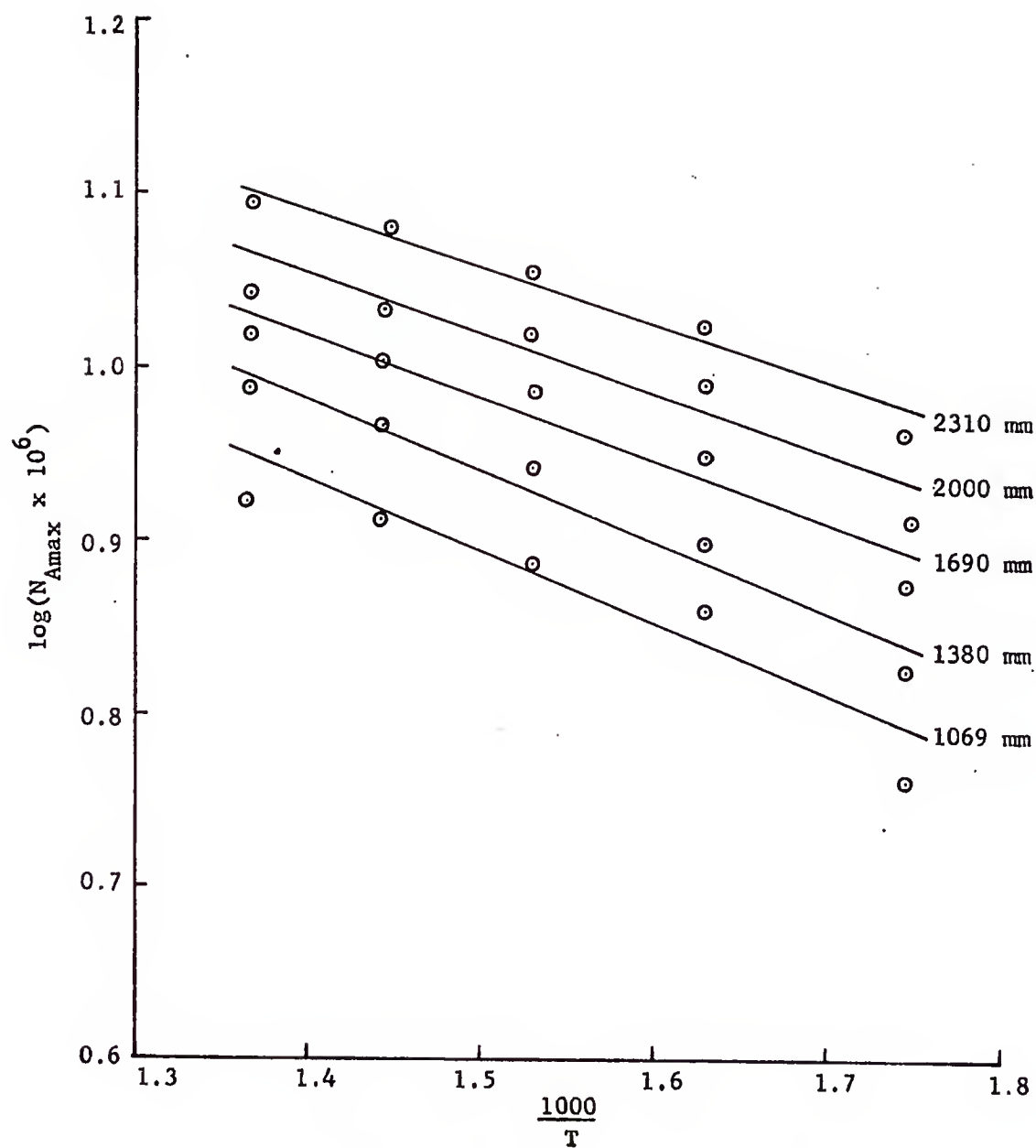


Figure 82. Determination of the Energy of Activation

Feed Gas Composition: 25.6% N₂, 74.4% H₂

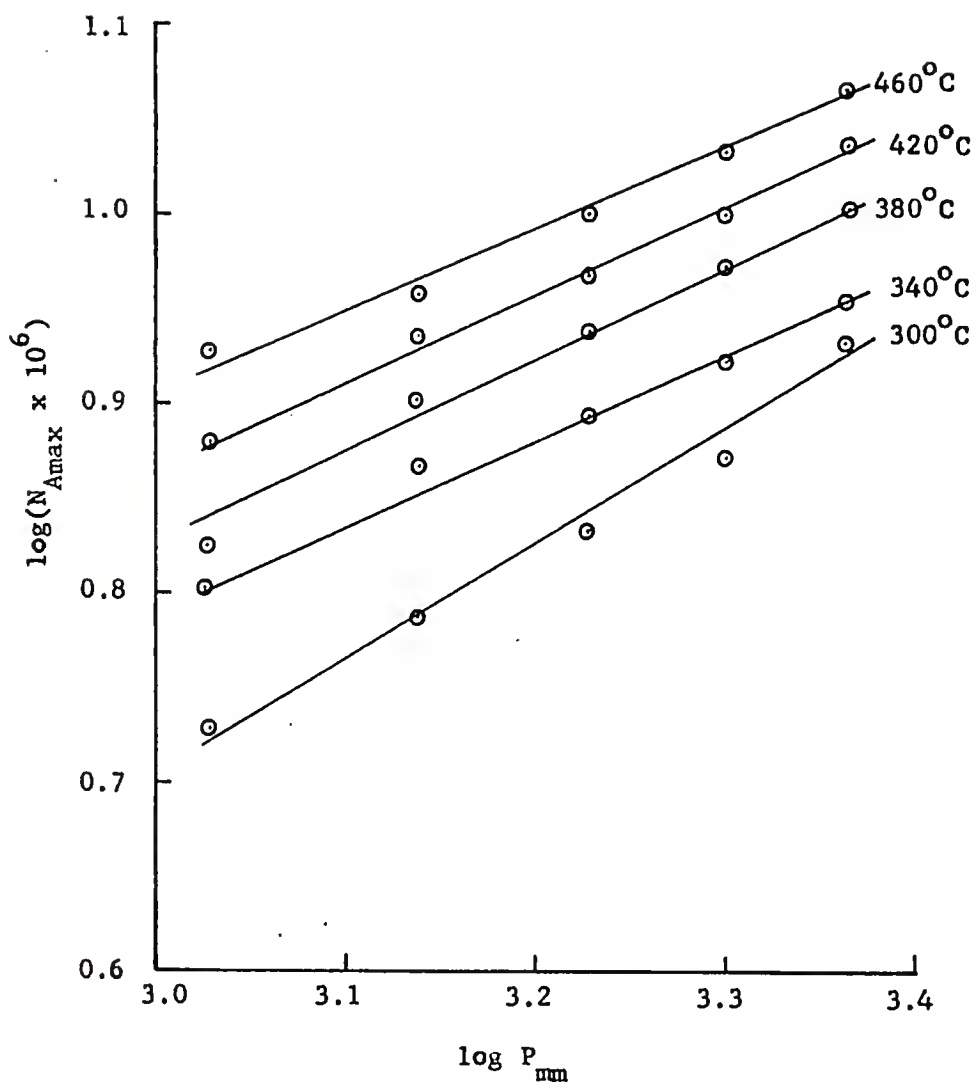


Figure 83. Effect of Impurities on the Maximum Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

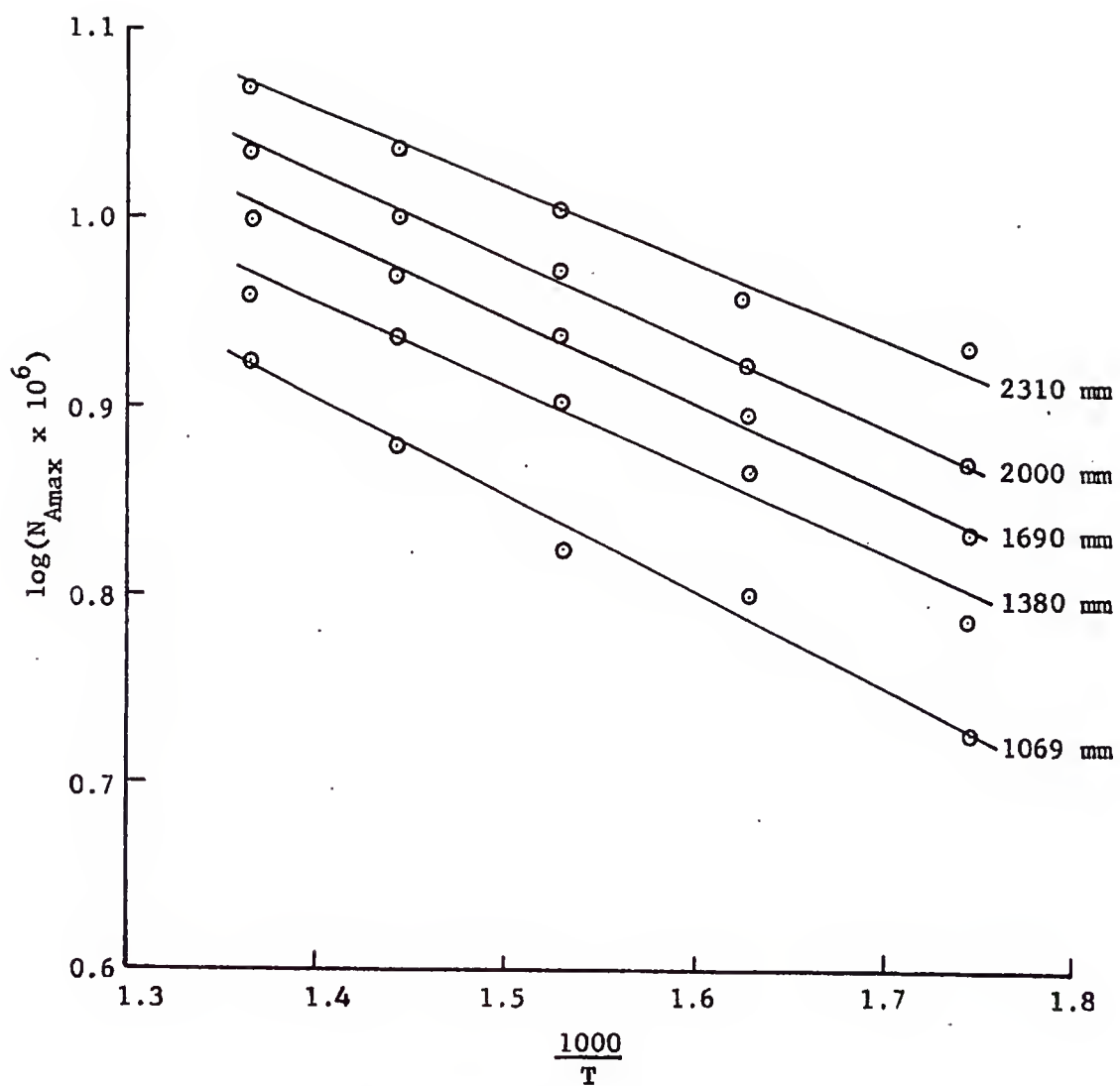


Figure 84. Determination of the Energy of Activation

Feed Gas Composition: 19.8% CH₄, 80.2% H₂

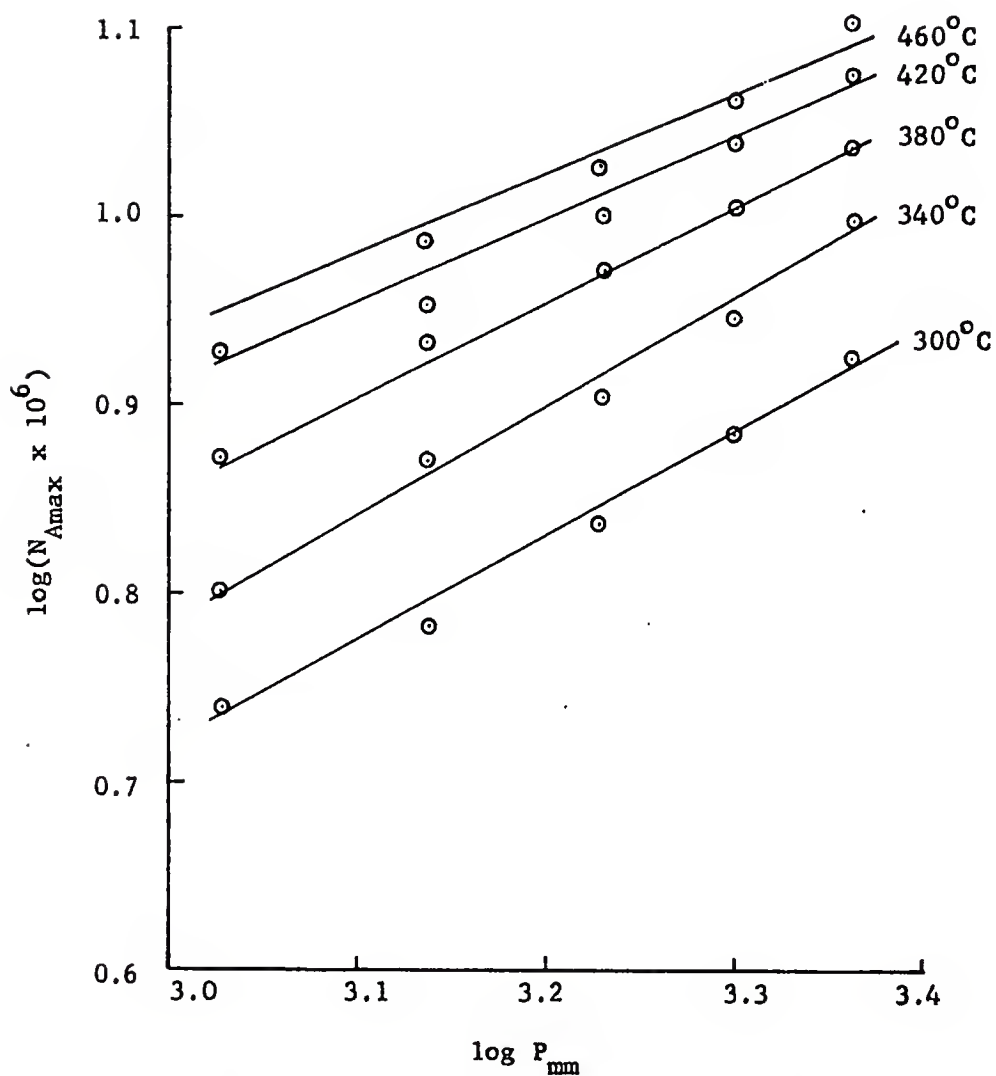


Figure 85. Effect of Impurities on the Maximum Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

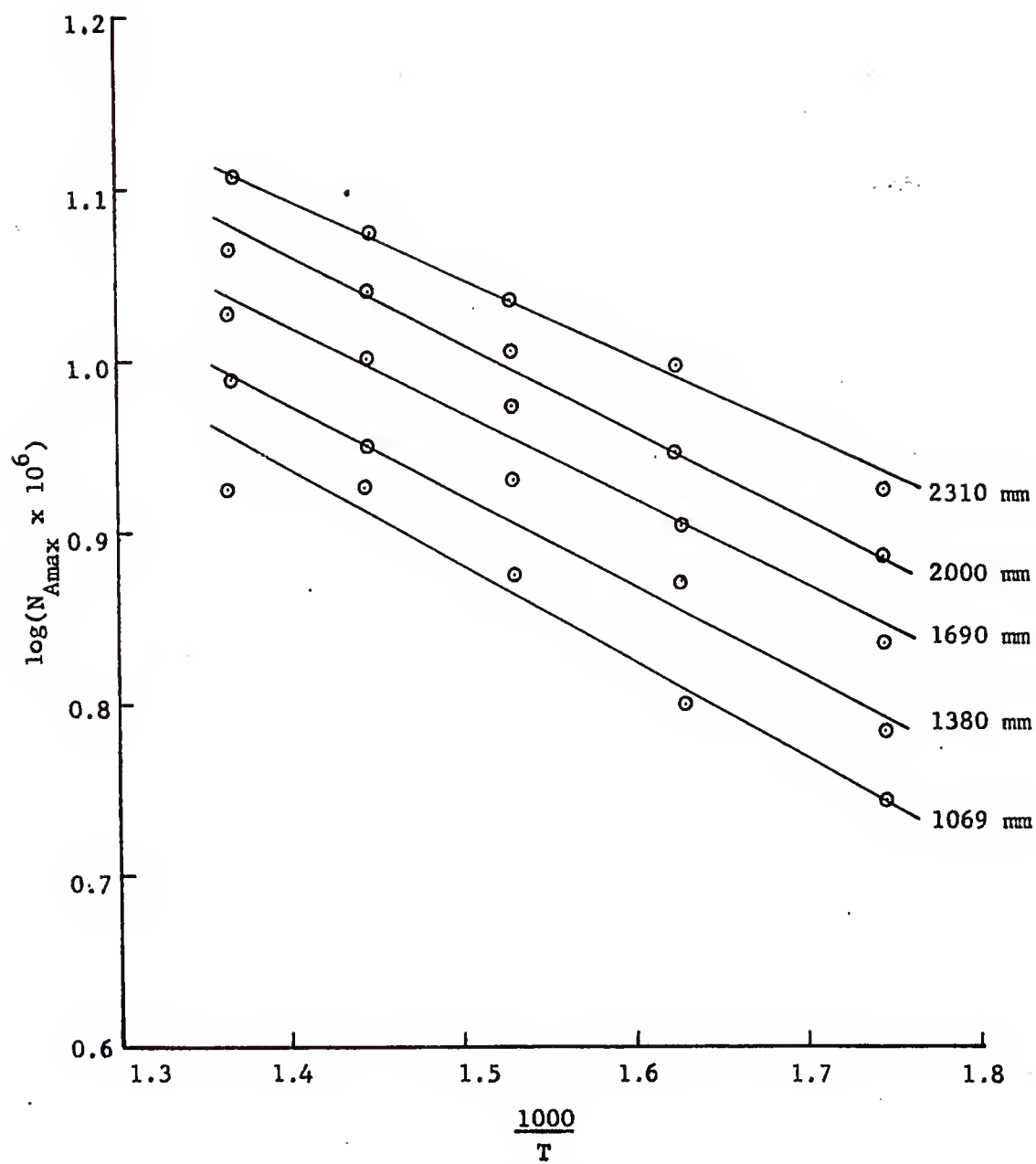


Figure 86. Determination of the Energy of Activation

Feed Gas Composition: 21.5% CO₂, 78.5% H₂

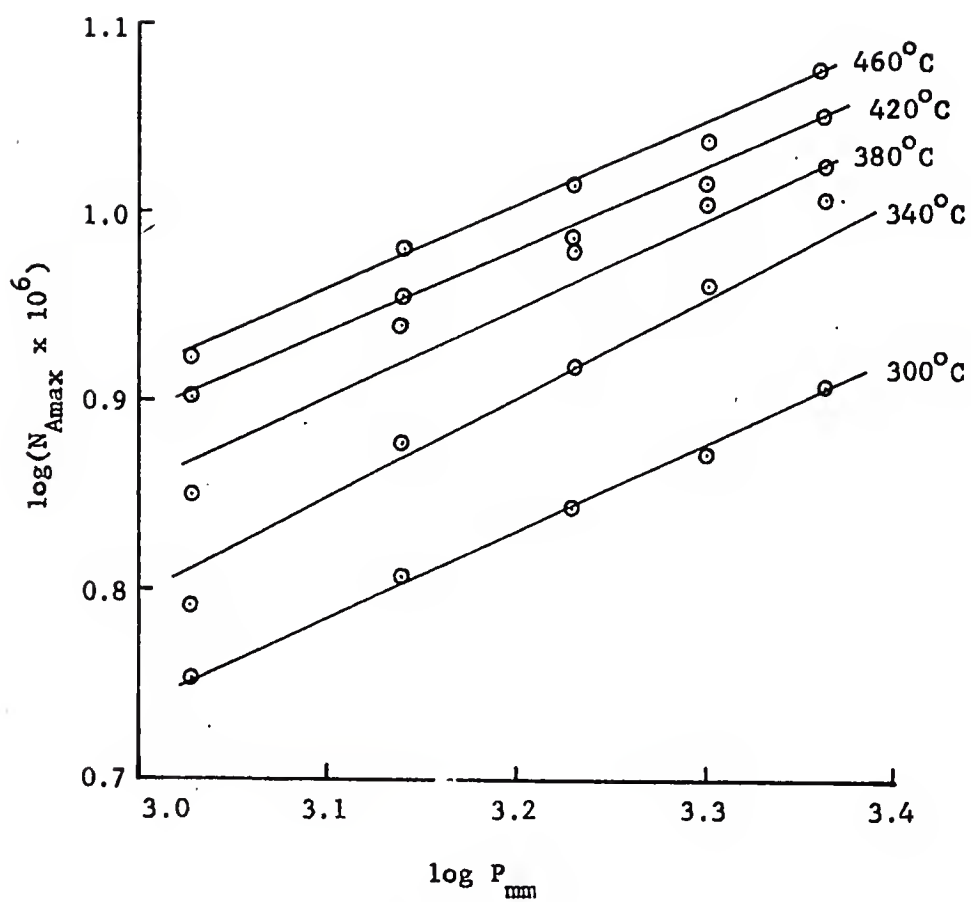


Figure 87. Effect of Impurities on the Maximum Rate of Transport of H₂ Through Pd-Ag Membrane at Different Temperatures

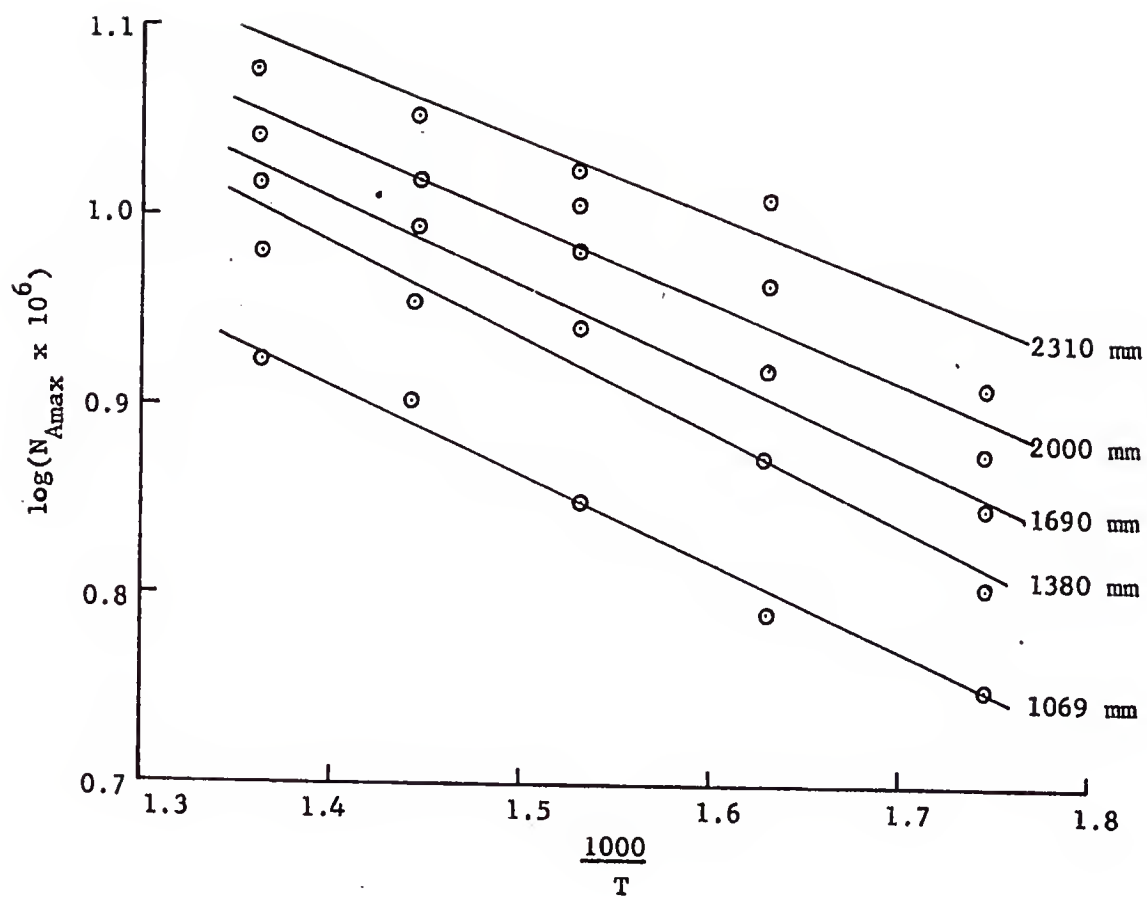


Figure 88. Determination of the Energy of Activation

TABLE 29

MULTIPLE REGRESSION OF THE CONSTANT IN EQUATION (108)
FOR THE MAXIMUM TRANSPORT RATE

<u>Feed Gas Composition</u>	<u>k_1</u>	<u>k_1'</u>	<u>$\frac{1}{n}$</u>	<u>$\frac{\Delta E}{R}$</u>
30% CH ₄ , 10% N ₂ , 60% H ₂	1.1×10^{-6}	8.5×10^{-7}	0.50	-1160
10% CH ₄ , 10% N ₂ , 80% H ₂	8.0×10^{-7}	7.2×10^{-7}	0.51	- 850
25.6% N ₂ , 74.4% H ₂	1.1×10^{-6}	9.4×10^{-7}	0.48	- 990
19.8% CH ₄ , 80.2% H ₂	1.1×10^{-6}	9.8×10^{-7}	0.52	-1140
21.5% CO ₂ , 78.5% H ₂	1.2×10^{-6}	1.1×10^{-6}	0.48	-1000

The observed value of the energy of activation shows that carbon monoxide has the largest energy of activation followed by methane, carbon dioxide and nitrogen. In Chapter II it was pointed out that gases which have the largest heat of adsorption have the longest residence time at the surface. The longer the residence time of the impurities in the surface, the greater will be the energy of activation. Therefore if the heats of adsorption of the impurities were known, the energy of activation of the transport process would fall in the same sequence as the heats of adsorption. It is also observed, as might be expected, grease lowers the transport rate.

E. Time to Reach Steady State

The time to reach 80% steady state in the experiment varies from a few seconds to less than two minutes. This is in the range that is expected by using Equations (81) and (99).

CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSIONS

A. Transport Rate of Pure Hydrogen Through Palladium-Silver Membranes

The transport rates found in this study are several times greater than those observed by most earlier investigators. This is to be expected for several reasons. In Chapter II it was pointed out that in the α -phase region hydrogen is more soluble in palladium-silver alloys than in pure palladium. The reverse is true for the β -phase region. Hurlbert and Konecny (5) employed pure palladium membranes whereas palladium-silver membranes were used in this investigation. Since all of this work was done under conditions where the hydrogen concentrations were relatively small, it is easily seen that the hydrogen transport rate through the membrane should be higher for the alloy than for pure palladium. Kydonius (33) did not bleed his gas, and it seems likely that his transport rates were lowered by the presence of accumulated impurities on the upstream side of the membrane.

The experimental transport rate data correlate very well with an equation containing a term $p^{1/n}$ where $\frac{1}{n}$ has an average value of 0.62. This is approximately the average of the values of the slopes of the isotherms shown in Figure 17. Kydonius, using the same kind of membrane but at lower temperatures, obtained a value of $\frac{1}{n}$ about 0.70.

The energy of activation found in this work is lower than that found by previous investigators. Their values range from 2.5 to 36 kcal/mole. The energy of activation based on the transport rate is an overall activation energy, and, if adsorption or dissociation

contributes to the transport process (such as is the case when impurities are present) ΔE should be greater than that for diffusion alone. Thus, large energies of activation strongly suggest that surface processes are rate limiting.

Bleeding, therefore, appears to accomplish two things: firstly, it dilutes the impurities present at the upstream face of the membrane; secondly, it should result in a lower energy of activation since it would tend to reduce the number of adsorption sites occupied by impurity molecules. There may be a thermal effect also. The incoming feed gas is approximately at room temperature while the palladium-silver membrane is at a higher temperature, and the difference in temperature would be sufficient to cause convection. Moreover, since the cooler molecules have lower velocities, the rate at which they strike unit area of surface would also be decreased as compared to a hot gas. However, the diffusion rate in the gas phase is so high that this effect appears to be negligible.

The calculation of the diffusivity for the palladium-silver gives a value which is slightly lower than that for pure palladium. This is to be expected since hydrogen does not diffuse rapidly through silver.

B. Effect of Impurities on the Transport Rate of Hydrogen Through Palladium-Silver Membrane

As shown in Figures 19 to 52, the introduction of impurities into hydrogen lowers the transport rate. This can be attributed to the following effects: (1) hydrogen is diluted by the impurities; (2) impurities hinder the diffusion of hydrogen in the gas phase;

(3) occupation of adsorption and dissociation sites by impurities result in a reduction of hydrogen adsorption and dissociation. The overall effect of impurities is, therefore, to lower the concentration of hydrogen atoms in the upstream surface of the palladium-silver membrane, and since the diffusion rate in the alloy is directly proportional to concentration, the transport rate decreases.

It is natural to assume that good mixing occurs in the upstream cavity of the diffusion cell. If this is the case, and there are no surface effects, then Equation (C-8) of Appendix C should hold. This was found not to be true, since Equation (115) rather than Equation (C-8) fits the data. This implied that two regions exist in the upstream side, (1) a region where plug flow exists, and (2) a region near the membrane where an impurity-rich layer is formed. This layer constitutes a resistance to diffusion from the gas phase to the surface of the membrane and leads to the postulation of a hypothetical mass transfer coefficient, k_G , based on gas film resistance. The mass transfer coefficient was found to be directly proportional to the bleed rate, as shown by agreement of the data with Equation (121). Since the mass transfer coefficient is inversely proportional to the gas film resistance, bleeding the feed gas reduces the gas film resistance.

The multiple regression analysis of Equation (108) for N_A and N_{Amax} shows that $\frac{1}{n}$ is generally smaller when impurities are introduced; an exception is grease. This is possibly caused by the occupation of adsorption sites for hydrogen by impurities. Gases such as CH_4 , N_2 , and CO_2 appear to be physically adsorbed on palladium-silver; gases such as CO appear to be chemisorbed, and may occupy most of the dissociation

sites for hydrogen. It can be deduced from Chapter II that these gases have a larger residence time on the membrane than hydrogen. Since increasing the total pressure increases the concentration of both hydrogen and impurities in the gas phase, and since the impurities have a longer residence time than hydrogen, the effect of the impurities is greater than one would predict from low mole fraction, and greater at high pressures than at low pressures. This lowers the value of $\frac{1}{n}$ when compared with a feed gas of pure hydrogen.

The multiple regression analysis for N_A and N_{Amax} also shows that the energy of activation for diffusion is higher when impurities are introduced. Since the energy of activation is based on the overall transport rate, it is really an overall activation energy. If the impurities adsorb at surface of the membrane, it would increase the energy of activation above that observed for pure hydrogen, and it is to be expected that a gas which chemisorbs will have a higher energy of activation than one which is physically adsorbed. Gases with unsaturated double bonds were found to have a higher energy of activation for diffusion than chemically inactive gases, such as N_2 .

The transport rate of hydrogen containing carbon monoxide as an impurity is greatly reduced when the temperature is between 300°C to 380°C ; at higher temperatures, i.e., from 420 to 460°C this system behaves essentially the same as systems with inactive gas impurities. The large decrease of the transport rate in the temperature range 300°C to 380°C suggests a poisoning effect of the carbon monoxide similar to that of hydrogen sulfide observed by other investigators (5).

It also indicates that most of the adsorption and dissociation sites for hydrogen are occupied by carbon monoxide. However, sulfide poisoning is stronger, since it permanently damaged the membrane once poisoned by hydrogen sulfide. Whereas, the poisoning effect of carbon monoxide is removed by raising the temperature to 420°C . This suggests that the bond formed between palladium and carbon monoxide at the low temperatures is unstable at higher temperatures.

C. Conclusion

The equation for the transport of hydrogen through palladium, i.e., Equation (112), fits the experimental data quite well, but the transport rates observed differ by a factor of 2 or 3 from those obtained by recent investigators. Compared with some investigators in the past, for which the transport rate varied as much as 1000 times, this agreement is fairly reasonable.

Equation (112) is an approximation of a more complicated equation, but is reasonably good for a given range of conditions.

Introduction of impurities lowers the transport rate either by the dilution effect of the nondiffusing component in the gas phase or by a surface effect, or both. The surface effect is caused by the reduction of adsorption sites and dissociation sites of hydrogen by the impurities, resulting in a reduction of the absorbed hydrogen atom concentration just inside the upstream membrane surface. If the surface effect is so large that it becomes the rate-limiting process in the transport of hydrogen through palladium, it is said that the impurities poison the membrane. This is probably caused by the

chemisorption of impurities at the surface or by the chemical reaction of the impurities with the surface atoms. Carbon monoxide and grease poison the membrane over the temperature range of 300°C to 380°C , but appear not to do so at temperatures above 420°C . If the surface effect is small, such as in the case of CH_4 , CO_2 , and N_2 , it is believed that only physical adsorption of the impurities occur at the surface.

When impurities are introduced and the feed gas is bled, Equation (115) fits the experimental data quite well. This equation combined with Equation (112) for expressing N_{Amax} fit the experimental data for a wide range of bleed rate, temperature, and pressure. Equation (115) suggested that there exists an impurity rich gas film near the surface of the membrane. Comparing N_{Amax} with that for the transport rates of pure hydrogen on the same basis and conditions indicates that N_{Amax} is lower than that for pure hydrogen. Furthermore, the multiple regression analysis of N_{Amax} shows that the value of $\frac{1}{n}$ is lower and the energy of activation is higher than that for pure hydrogen. All this suggests that surface effect is present when impurities are introduced.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDIES

In this study, no positive confirmation as to the exact nature of the reaction between the metal and poisoning gas has been established. In the light of the development of recent analytical methods, it may be possible to determine the nature of the bond between the metal and poison.

The effect of silver content on the diffusivity can also be examined more extensively. This would lead possibly to the study of the order-disorder phenomena in the palladium-silver alloy. The assumption in this work is that palladium-silver atoms are completely random or disordered. An investigation of the effect of other impurities than those studied here is also recommended.

The effect of cell construction, annealing procedures of the membrane, and repeated cycling to determine membrane stability and transport efficiency are also some of the areas which need further study.

NOMENCLATURE

a	lattice constant; constant in Equation (27)
$a_H(T)$	the partition function for the internal degree of freedom of an absorbed hydrogen atom referred to the ground state at infinite separation
A	area of membrane
B	bleed rate
C, C_1, C_o	concentration
C_A	concentration of A
C_1, C_2	constant of integration in Equation (74)
D	diffusivity
D_o	constant defined by Equation (53)
E_H	ϵ_H in the molal basis
E_{HH}	ϵ_{HH} in the molal basis
E_D	ϵ_D in the molal basis
ΔE	energy of activation
ΔE_D	energy of activation of diffusion
$E(X-Y)$	bond energy between X and Y
f_r	geometric factor
F	Helmholtz free energy
ΔF^f	free energy of formation
$\Delta F^\ddagger$	free energy of activation
$g(N_H, N_{HH})$	total number of distinguishable configuration of N_H atoms
h	Planck constant
ΔH	heats of adsorption
ΔH_c	heats of solution

k	Boltzmann constant
k_1, k_1', k_2, k_3, k_4	constants
k_g', k_g	hypothetical mass transfer coefficient
K	equilibrium constant
$K(T), K'(T)$	constant defined by Equation (17); $K(T)$ in molal basis
L	thickness of membrane
M	mean molecular weight per constituent atom
M_H	atom mass of hydrogen
M_I	moment of inertia of the hydrogen atom
$n(x)$	the number of diffusing particles per cm^2 on the plane located at x at the instant t
n_1, n_2	gram moles of hydrogen at the start and at time ϕ respectively
N_A	molal flux of A
N_H	number of hydrogen atoms in the lattice
N_S	number of interstitial sites
N_{HH}	number of pairs of neighboring hydrogen atoms in a particular configuration
$\bar{N}_{HH}$	defined by Equation (8)
$\bar{N}$	defined by Equation (2)
$P, \bar{P}$	pressure
$P\left(\frac{1}{2}\right)$	equilibrium pressure of the α - β phase transition
P_i, P_f	downstream pressure at the start of the experiment and at time ϕ respectively
ΔP	$P_f - P_i$
P_r	probability for a given interstitial hydrogen to make a jump per second
q	defined by Equation (75)

$q_H(T)$	partition function for vibration of absorbed H atom relative to the lattice
q_0	the initial heat of adsorption
Q	partition function
Q^+	partition function of the normal state
$Q^\ddagger$	partition function of the activated state
R	gas constant
R_A	chemical reaction rate of A
ΔS	entropy of activation
SST	fraction of the steady state value approach at dimensionless time τ
t	time
T	temperature
T_s, T_m	melting temperature
T_c	critical temperature
v	defined by Equation (66)
v^*	molar average velocity
V	molar volume; Laplace transform of v
X_{Ag}	weight fraction of silver
z	number of nearest neighbors

Greek Letters

β	constant
ϵ_{HH}	total interaction energy at saturation per atom
$-\epsilon_H$	the energy required to remove an absorbed H atom, far removed from any other absorbed H atom, from its lowest state in the metal to rest at infinite dispersion

ϵ_D	energy required to dissociate a hydrogen molecule from its lowest state into two free atoms in its lowest state
θ	fraction of interstitial sites occupied
λ_H	absolute activity
λ	distance between two atomic planes where diffusing is occurring
μ	chemical potential
μ_x	electronegativity
ν	frequency of vibration of linear oscillator
ρ	spin weight of the proton
τ	adsorption residence time
τ	dimensionless time in Equation (81) and Equation (99)
τ_0	constant defined by Equation (36)
ϕ	time

LITERATURE CITED

1. Graham, T., Proc. Roy. Soc. (London), 15, 502 (1868).
2. Lombard, V. and Eichner, C., Bull. Soc. Chim. (France), (4), 53, 1194 (1933).
3. Silberg, P. A. and Bachman, C. H., J. Chem. Phys., 29, 777 (1958).
4. Jaumont, Frank E., Jr., A Bibliography of Diffusion of Gases, Liquids and Solids in Solids, 1890 to 1955, AEC Report T1 D - 3071.
5. Hurlbert, R. C. and Konecny, J. O., J. Chem. Phys., 34, 655 (1961).
6. DeRosset, A. J., I.E.C., 52, 525 (1960).
7. Darling, A. S., Platinum Metals Rev., 2, 16 (1958).
8. Lombard, V. and Eichner, C., Bull. Soc. Chim. (France), (4), 51, 1462 (1932); (4), 55, 945 (1934); (5), 2, 1555 (1935); (5), 3, 2203 (1936); (5), 4, 1276 (1937).
9. Derrig, Joseph P., "The Purification and Production of Hydrogen by the Palladium Diffusion Process," presented at American I. Ch. E. 49th National Meeting, New Orleans, La., March, 1963.
10. McBride, R. B. and McKinley, D. L., Chem. Eng. Prog., 61, 81 (1965).
11. Lederer, L. and Greene, N. D., Electrochim. Acta, 8, 883 (1963).
12. Sieverts, A. and Bruning, H., Z. Physik. Chem., A163, 409 (1933).
13. Sieverts, A. and Hagen, H., Z. Physik. Chem., A174, 247 (1935).
14. Sieverts, A. and Zapf, G., Z. Physik Chem., A174, 359 (1935).
15. Norberg, R. E., Phys. Rev., 86, 745 (1952).
16. Isenberg, I., Phys. Rev., 79, 736 (1950).
17. Mott, N. F. and Jones, H., "The Theory of the Properties of Metals and Alloys," Dover Publications, Inc., New York, pp. 200 (1958).
18. Gillespie, L. J., Galstaun, L. S., J. Am. Chem. Soc., 58, 2565 (1936).

19. Nace, P. M. and Aston, J. G., J. Am. Chem. Soc., 79, 3619 (1957).
20. Ibid, 3623.
21. Lacher, J. R., Proc. Roy. Soc. (London), A161, 525 (1937).
22. Libowitz, G. G., J. Appl. Phys., 33, 399 (1962).
23. Makrides, A. C., Final and Summary Report, Contract DA-49-186-ORD-982, July, 1964; Axelrod, S. D. and Makrides, A. C., J. Phys. Chem., 68, 2154 (1964); Makrides, A. C., J. Phys. Chem., 68, 2160 (1964); Jewett, D. and Makrides, A. C., Trans. of the Faraday Soc., 61, 933 (1965).
24. Vert, H. L., Mosevich, I. A. and Tverdovskii, I. R., Proc. Acad. Sci. U.S.S.R., Phys. Chem. Sect., 140, 662 (1961).
25. Salmon, O. N., Randal, D. and Wilk, E. A., Mechanism of the Diffusion of Hydrogen Through Active and Inactive Palladium, AEC Research and Development Report, KAPL-1674 (1956).
26. Davis, W. D., Diffusion of Gases Through Metal, AEC Research and Development Report, Part I, KAPL-1227, Part II, KAPL-1375.
27. May, J. W., I.E.C., 57, 19 (1965).
28. de Boer, J. H., "The Dynamical Character of Adsorption," Oxford University Press, Great Britain (1953).
29. Trapnell, B. M. W., "Chemisorption," London, p. 243, Butterworths Scientific Publications.
30. Pauling, L., "The Nature of Chemical Bond," New York, Cornell University Press (1960).
31. Simons, J. H. and Ham, W. R., J. Chem. Phys., 7, 899 (1939).
32. Smith, D. P., Gases in Metal, Am. Soc. for Metals, Cleveland, Ohio (1953).
33. Kydonius, A. F., University of Florida Ph.D. Dissertation, December, 1964.
34. Kussner, A., Z. Physik Chem., 36, 383 (1963).
35. Krivoglaz, M. A. and Smirnov, A. A., "The Theory of Order-Disorder In Alloys," American Elsevier Publishing Company, Inc., New York (1964).
36. Eyring, H. and Glasstone, S., "The Theory of Rate Processes," New York and London, McGraw-Hill (1941).

37. Fowler, R. H. and Guggenheim, E. A., "Statistical Thermodynamics," New York, The MacMillan Co., Cambridge University Press (1956).
38. Fowler, Proc. Camb. Phil. Soc., 32, 144 (1936).
39. Lewis, F. A., Plat. Metals Rev., 5, 21 (1961).
40. Dekker, A. J., "Solid State Physics," New Jersey, Prentice-Hall, Inc., pp. 70 (1959).
41. Wert, C. A., Physical Review, 79, 601 (1950); Wert, C. A., Journal of Applied Physics, 21, 1196 (1950); Wert, C. A. and Ziner, C., Physical Review, 76, 1169 (1949).

APPENDICES

APPENDIX A

APPARATUS

Diffusion Cell: Type 316 Stainless Steel

Chemical Engineering Department, University of
Florida, Gainesville, Florida

Electric Furnace: 1400 Watts. Maximum Temperature 1950°F

Fisher Scientific Company, Pittsburgh, Pennsylvania

Thermocouple Vacuum Gauge: Type GTC-100. 0-1000 Microns Range

Consolidated Vacuum Corporation

Rochester, New York

Temperature Controller: CHR. AL. Thermocouple, Series 60 Control

Leeds and Northrup, Philadelphia, Pennsylvania

Timer: Range 0.1-9999.9 Seconds

Precision Scientific Co., Chicago, Illinois

Vacuum Gauge: Range 0.0001-25 mm, Mcleod Vacuum Gauge

Todd Scientific Co., Springfield, Pennsylvania

Duo-Seal Vacuum

Pump: Welch Series 1400B, Duo-seal Vacuum Attainable, 0.1 Micron

W. M. Welch Manufacturing Company, Chicago, Illinois

Safety Relief Valve: Model No. 21, Max. Pressure 50 psig

The Matheson Company, Inc., East Rutherford,

New Jersey

Toggle Valve: Model 1254

Crawford Fitting Co., Cleveland, Ohio

Metering Valve: Model 2PY 280 Metering Valve with Vernier Handle

Hoke, Inc., Cresskill, New Jersey

Flow Meter: Model 995 Bantam Flo-Gages-5-100 cc/mm of Carbon Dioxide

Hoke, Inc., Cresskill, New Jersey

Pressure Gauge: 30"-100 psig

U. S. Gauge, Sellersville, Pennsylvania

Fittings and Tubing: 1/8" to 1/4" fittings and tubing

Crawford Fitting Co., Cleveland, Ohio

Silver Palladium Foil: 6" x 6" x 0.004" Pd. 25% Ag Foil

Engelhard Industries, Newark, New Jersey

APPENDIX B

EXPERIMENTAL PROCEDURE

A. Preparation of the Palladium-Silver Membrane

1. Soak the palladium-silver membrane and copper gaskets in ether for one hour, rinse twice with distilled water and drip.
2. Mount the palladium-silver membrane and copper gaskets in the diffusion cell.
3. Evacuate both sides of the membrane by opening valve V4, V5, V7, V8, V9, and V11. All other valves being closed. Heat to 460°C for one hour while being continuously evacuated. Cool to 300°C while continuously evacuating.
4. When a temperature of 300°C is reached, close valve V4 and open valve V2 with pressure set at 1069 mm Hg. Then adjust valve V6 so that it reads a specific bleed rate in the flowmeter. Maintain this condition for one hour.
5. Change pressure to 2310 mm Hg and maintain other variables at same valves for one hour.
6. Change pressure to 1069 mm Hg and heat to 460°C for one hour. All other variables maintain at the same valves.
7. Repeat step 5.
8. The palladium-silver membrane is now ready for the experiment. If in subsequent use the bolts become loose, the cell is dismounted at both connectors and the bolts are tightened.

B. Procedure A

1. Evacuate both sides of the membrane and heat to 460°C for

one hour while continuously evacuating.

2. Cool to 300°C while continuously evacuating.

3. When the temperature reaches 300°C , close valve V4, open valve V2 with the pressure set at 1069 mm Hg, and adjust valve V6 so that the flowmeter reads the desired bleed rate. Maintain this condition for one hour.

4. Open valve V10 for 5 minutes and take reading of the initial pressure by the Mcleod Gauge. Set timer and close valve V10 and V11. After a suitable time interval, close valve V7 and open valve V10; take reading of the final pressure and time. The corrected final pressure is then obtained from Figure B-1. (This is necessary since the gas has expanded to the volume occupied by the Mcleod Gauge.)

5. Close valve V10, open valve V7 and V11, and change to the next higher pressure and adjust to the desired bleed rate. After 15 minutes repeat step 4.

6. Repeat step 5 until the pressure reaches 2310 mm Hg; then change pressure to 1069 mm Hg and heat to the next higher temperature for one hour.

7. Finally, repeat step 4 to step 6 until temperature of 460°C is reached.

C. Procedure B

1. Same as step 1 to step 3 of Procedure A.

2. Same as step 4 of Procedure A.

3. Close valve V10, open valve V7 and V11 and change temperature to the next higher value for one hour and repeat step 2.

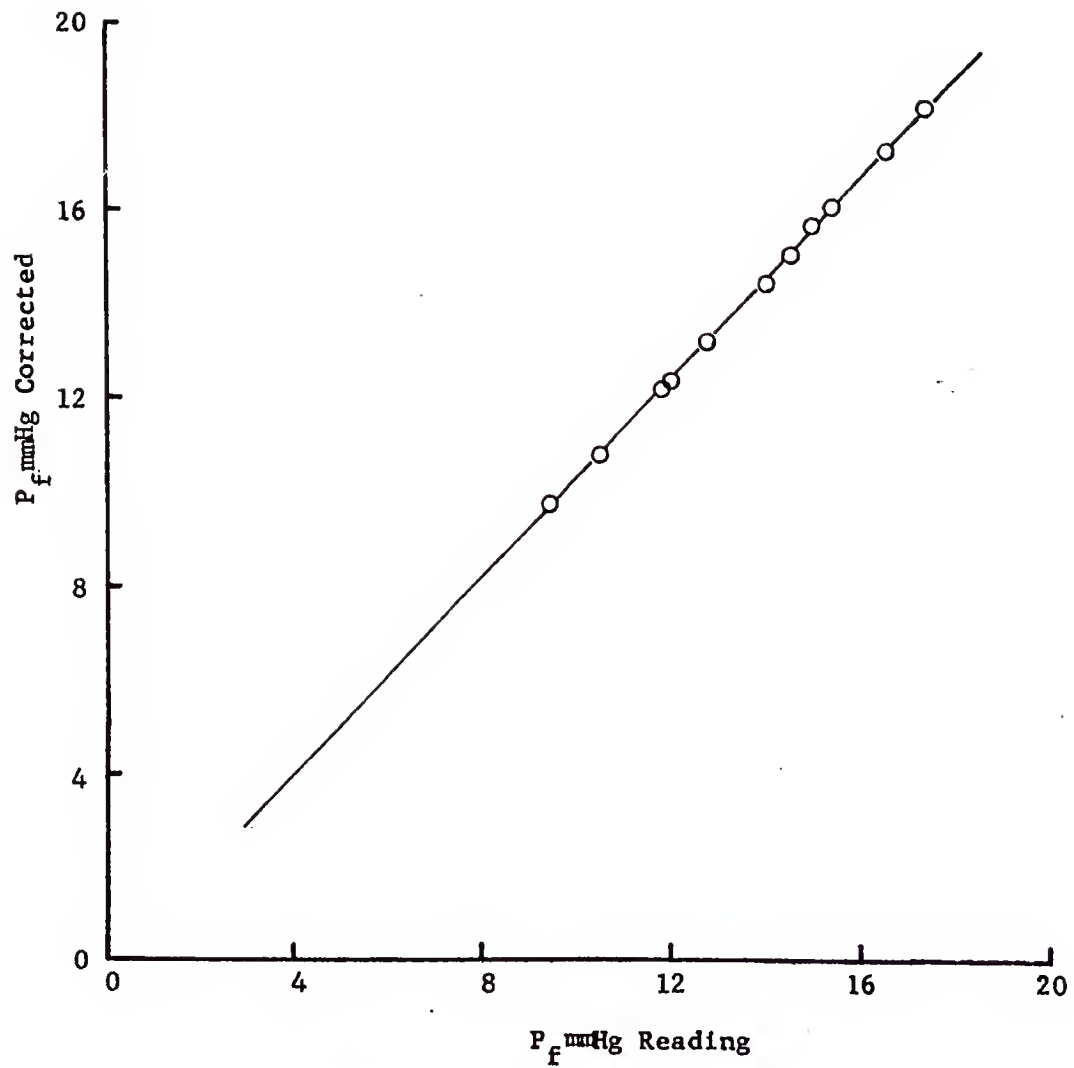


Figure B-1. Pressure Correction for the McLeod Gauge Reading

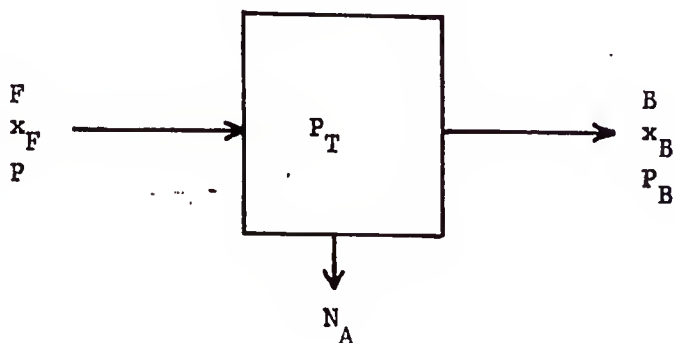
4. Repeat step 3 until 460°C is reached, then cool to 300°C .
5. When the temperature reaches 300°C , adjust the pressure to the next higher value; also adjust bleed rate to the desired value.
6. Repeat step 2 to step 5 until the pressure of 2310 is reached.

APPENDIX C

FLOW PATTERN IN THE DIFFUSION CELL

The assumption that perfect mixing occurs in the diffusion cell will be shown to be invalid for the case when Equation (115) applied to the experimental data.

Assuming that perfect mixing occurs in the diffusion cell, the material balance for the apparatus shown schematically below will be:



Where F = Feed rate/unit area

B = Bleed rate/unit area

N_A = Transport rate through membrane/unit area

x_F, x_B = Mole fraction of hydrogen in F, B respectively

P, P_B = Pressure of hydrogen in F, B respectively

P_T = Total pressure

The material balance gives

$$F = B + N_A \quad (C-1)$$

$$F x_F = B x_B + N_A \quad (C-2)$$

Eliminating F from Equations (C-1) and (C-2) gives

$$x_F(B + N_A) = Bx_B + N_A \quad (C-3)$$

But for perfect mixing and at constant temperature

$$\begin{aligned} N_A &= k'_1 \frac{1}{P_B} \exp\left(-\frac{\Delta E}{RT}\right) \\ &= k'_1 \frac{1}{P_B} \approx k'_1 \frac{1}{P_B} \end{aligned} \quad (C-4)$$

And from the ideal gas law

$$x_B = \frac{n_B}{n_T} = \left(\frac{P_B V}{RT}\right) \left(\frac{P_T V}{RT}\right) = \frac{P_B}{P_T} \quad (C-5)$$

where n_B = Gram moles of hydrogen in the bleed

n_T = Total number of gram moles of gases in the bleed

Therefore

$$N_A = k'_1 (P_T x_B)^{\frac{1}{2}} = k'' x_B^{\frac{1}{2}} \quad (C-6)$$

solving for x_B gives

$$x_B = k''' N_A^2 \quad (C-7)$$

Substituting the value of x_B from Equation (C-7) into Equation (C-3) and rearranging

$$N_A B = \frac{x_F}{k} \left(\frac{B}{N_A}\right) + \frac{x_W - 1}{k} \quad (C-8)$$

or

$$N_A B = k_{11} \left(\frac{B}{N_A}\right) + k_{22} \quad (C-9)$$

Thus Equation (C-9) is seen to differ from Equation (115).

This implies that perfect mixing does not occur in the diffusion cell, and that the actual flow situation lies somewhere between plug flow and perfect mixing.

BIOGRAPHICAL SKETCH

Leon L. Chiu was born on January 20, 1937, in Guinayangan, Quezon, Philippines. He received the degree of Bachelor of Science in Chemical Engineering in June, 1960 from the University of Santo Tomas.

He came to the United States in February, 1961, and enrolled in the Graduate School of the University of Florida. He received the degree of Master of Science in Engineering in April, 1963. Since then he has been working toward the degree of Doctor of Philosophy.

This dissertation was prepared under the direction of the Chairman of the Candidate's Supervisory Committee, and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April, 1966

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